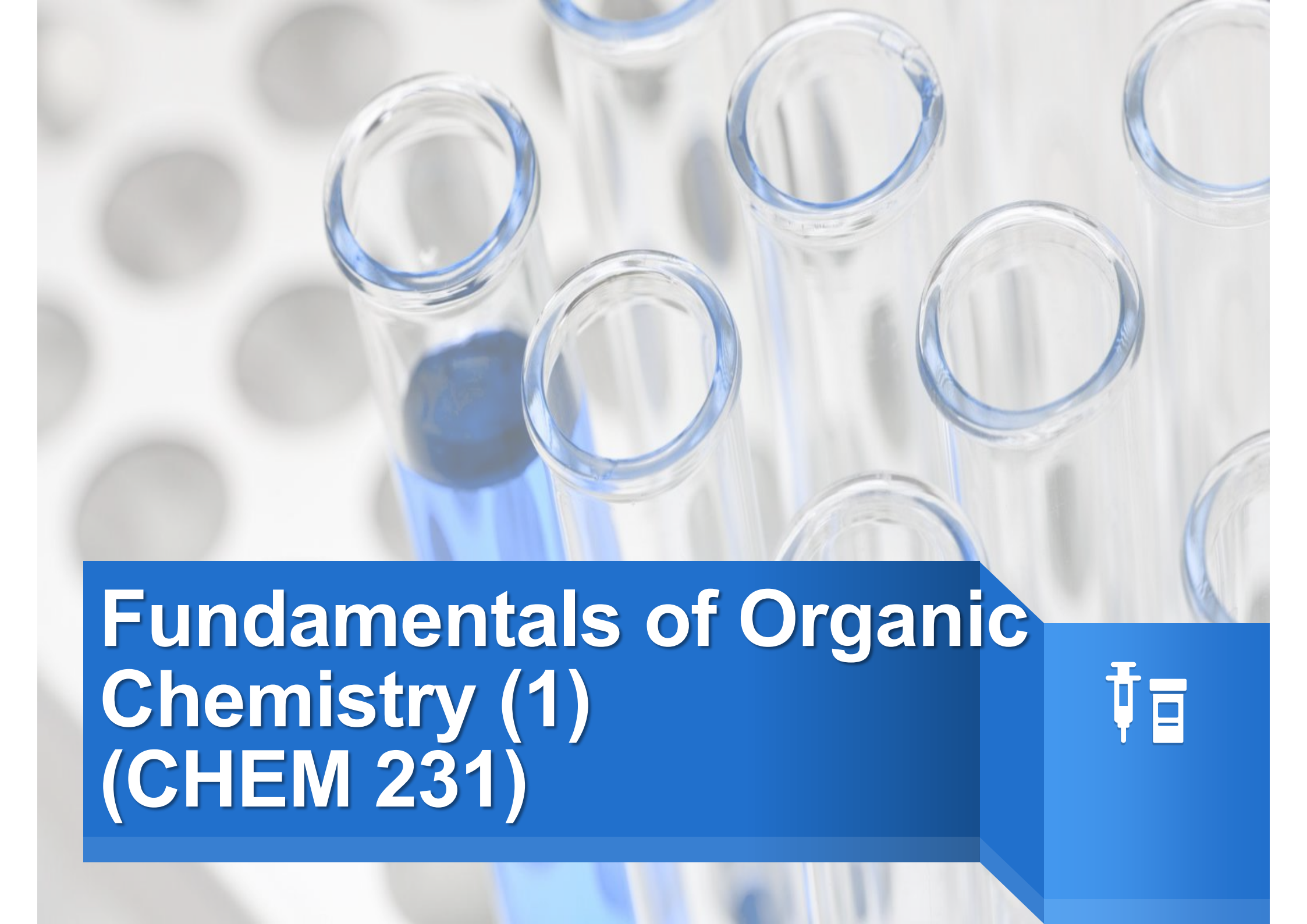




Fundamentals of Organic Chemistry (1) (CHEM 231)



Course Objectives:

“

- ▶ Giving the students an introduction about the chemical bonding.
- ▶ Explanation of important chemical reactions in aliphatic compounds.
- ▶ Identification of the functional groups.



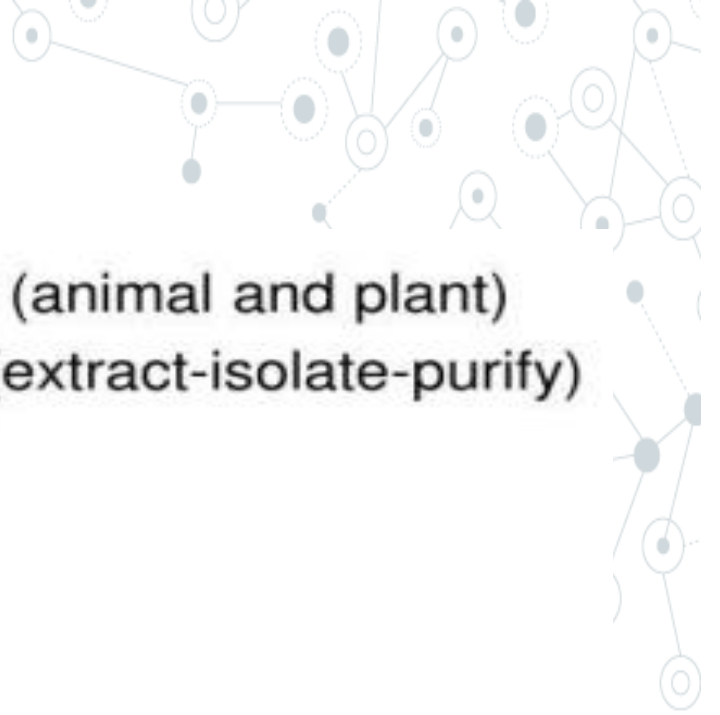
Giving the students an introduction about the chemical bonding.

1

Organic Chemistry: Definition

- The word **Organic** can be a biological or chemical term, in biology it means anything that is living or has lived. The opposite is Non-Organic.
- **Organic Chemistry** is unique in that it deals with vast numbers of substances, both natural and synthetic, **for example**: The clothes, the petroleum products, the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and drugs.
- **Organic chemistry** is defined as:
The study of carbon/hydrogen containing compounds and their derivatives.

Organic Compounds



Obtained by: { Isolation from nature (animal and plant)
(extract-isolate-purify)
Synthesis in lab

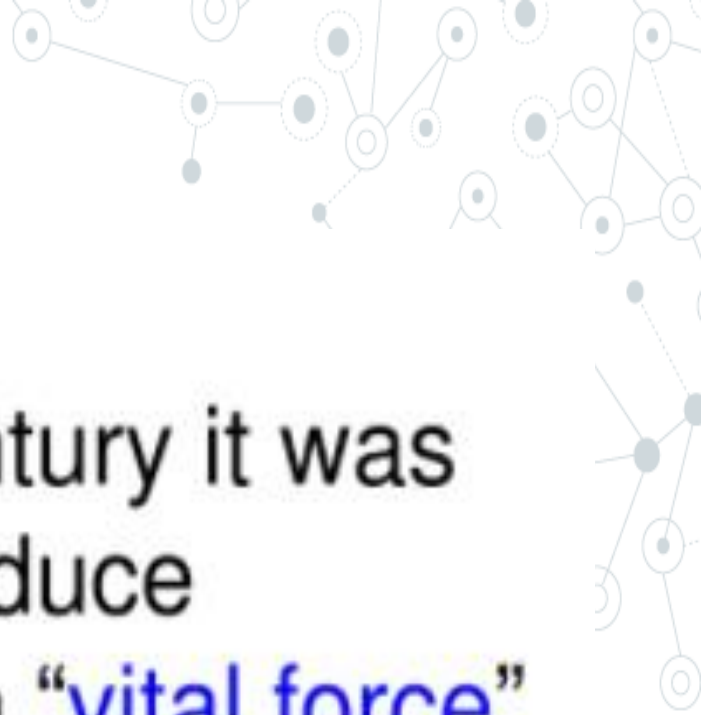
Organic compounds: 10 million

Inorganic compound: 1.7 million

Compounds in **living systems** are organic: **Biochemistry**



Organic Compounds



- History:
 - Earlier in the eighteenth century it was believed that in order to produce compounds by living cells, a “vital force” was needed.
 - These compounds were classified as organic compounds.
 - A german chemist, Friedrich Woehler in 1828 has shown this belief was incorrect
- 

Organic Compounds

Typical organic compounds:

- Contain carbon
- Have covalent bonds
- Have low melting points
- Have low boiling points
- Are flammable (all burn)
- Are soluble in nonpolar solvents
- May be gases, liquids or solids



Organic Compounds

XXXXX

Organic Compounds

Bonding is almost entirely covalent

May be gases, liquids, or solids with low melting points (less than 360°C)

Most are insoluble in water

Most are soluble in organic solvents such as diethyl ether, toluene, and dichloromethane

Aqueous solutions do not conduct electricity

Almost all burn

Reactions are usually slow

Inorganic Compounds

Most have ionic bonds

Most are solids with high melting points

Many are soluble in water

Almost all are insoluble in organic solvents

Aqueous solutions conduct electricity

Very few burn

Reactions are often very fast

The Uniqueness of Carbon

❖ What is unique about the element **carbon**?

❖ Why does it form so many compounds?

The answers lie in:

- ✓ The **structure** of the carbon atom.
- ✓ The **position** of carbon in the periodic table.

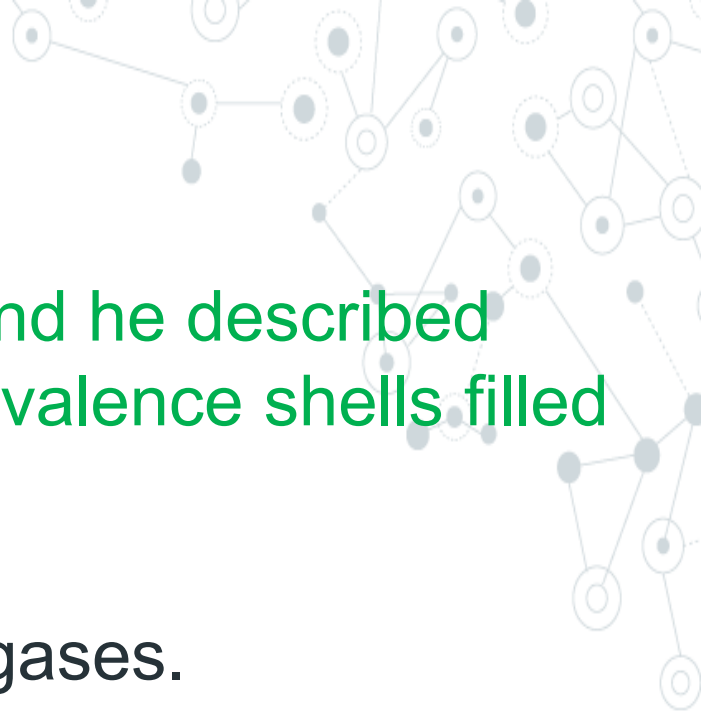
IA									Zero
H	IIA		IIIA	IVA	VA	VIA	VIIA	He	
Li	Be		B	C	N	O	F	Ne	
Na	Mg		Al	Si	P	S	Cl	Ar	
K	Ca	Transition Elements	Ga	Ge	As	Se	Br	Kr	
Rb	Sr		In	Sn	Sb	Te	I	Xe	
Cs	Ba		Tl	Pb	Bi	Po	At	Rn	
Fr	Ra								

❖ These factors enable it to form strong bonds with

- other carbon atoms
- and with other elements (hydrogen, oxygen, nitrogen, halogens,..etc).

➤ Each **organic compound** has its own characteristic set of physical and chemical properties which depend on the structure of the molecule.

Chemical Bonding



- **In 1916 G.N. Lewis** pointed out that:
 - The noble gases were stable elements, and he described their lack of reactivity to their having their valence shells filled with electrons.
 - **2 electrons** in case of helium.
 - **8 electrons** for the other noble gases.

□ **According to Lewis,**
in interacting with one another atoms can achieve a greater degree of stability
by rearrangement of the valence electrons to acquire the outer-shell structure of the closest noble gas in the periodic table.

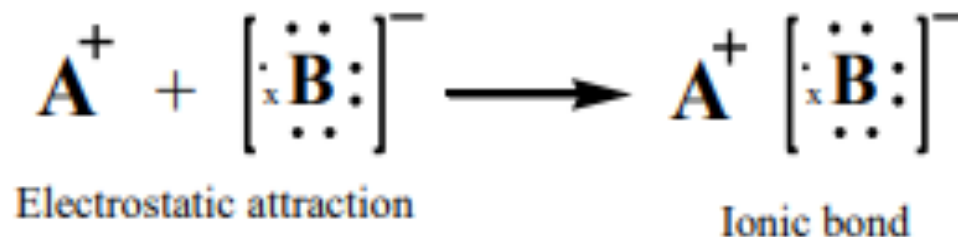
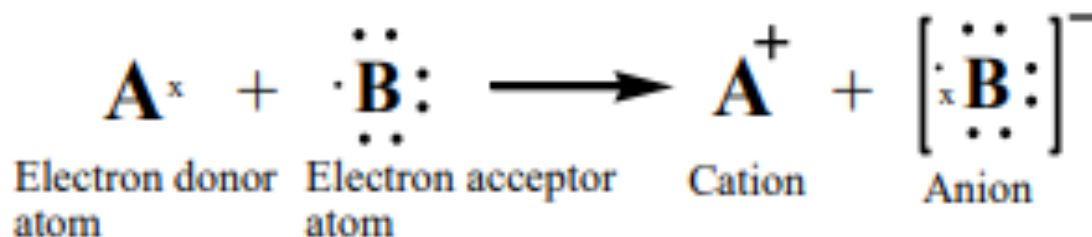


Chemical Bonding

A) Ionic Bonds

- Elements at the left of the periodic table give up their valence electrons and become +ve charged ions (**cations**).
- Elements at the right of the periodic table gain the electrons and become -ve charged ions (**anions**).

The electrostatic force of attraction between oppositely charged ions.



☐ Most ionic compounds are **inorganic substances**

Chemical Bonding

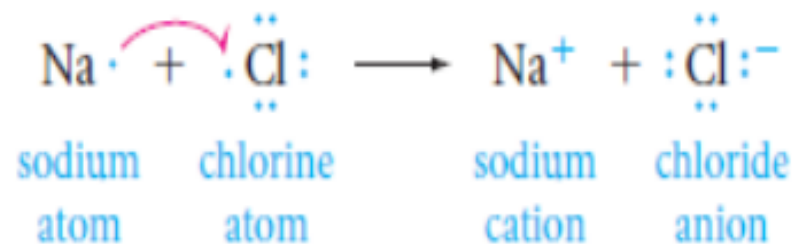
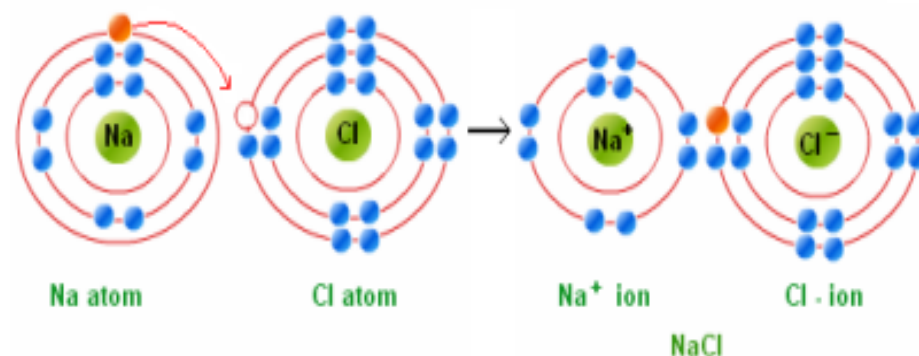
A) Ionic Bonds

Electronegativity Measures The Ability
of An Atom To Attract Electrons

Increasing Electronegativity							
H							
2.1							
Li	Be		B	C	N	O	F
1	1.5		2	2.5	3	3.5	4
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3
K							Br
0.8							2.8

Increasing Electronegativity

Example

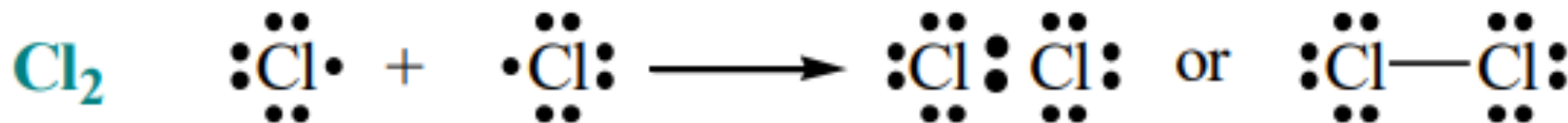
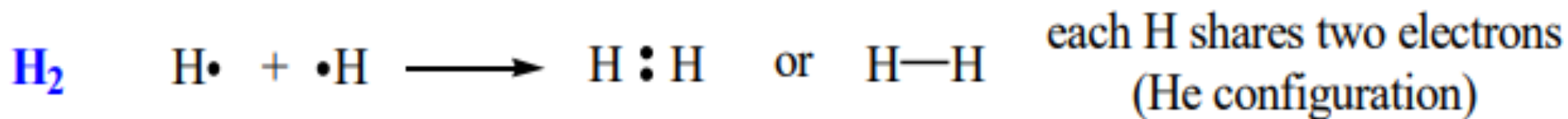


Chemical Bonding

B) Covalent Bonds

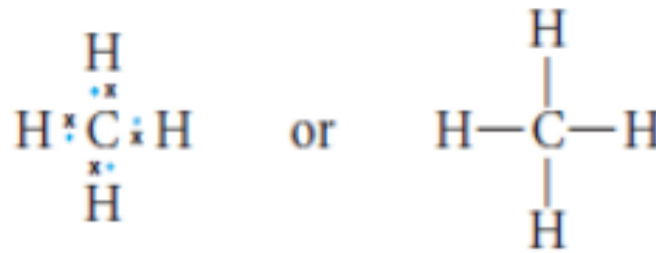
- Elements that are close to each other in the periodic table attain the stable noble gas configuration by sharing valence electrons between them.
- A shared electron pair between two atoms or single covalent bond, will be represented by a dash (-).
- **A covalent bond** involves the mutual sharing of one or more electron pairs between atoms.

❖ When the two atoms are identical or have equal electronegativities, the electron pairs are shared equally.

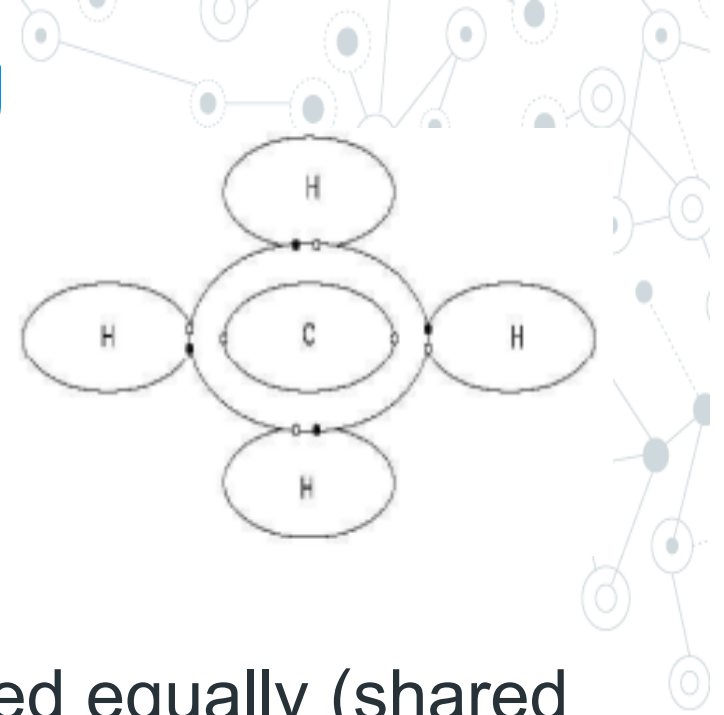


Chemical Bonding

B) Covalent Bonds



methane

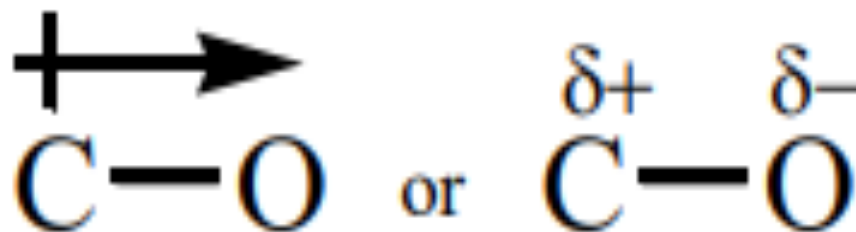


- When **two unlike atoms**;
the bonding electrons are no longer shared equally (shared unequally).

1) A Polar Covalent Bond

A bond, in which an electron pair is shared unequally.

- ❖ The more electronegative atom assumes a partial negative charge and the less electronegative atom assumes a partial positive charge.



Chemical Bonding

How Many Bonds to an Atom? Covalence Number

The number of covalent bonds that an atom can form with other atoms.

i.e. the covalence number is equal to the number of electrons needed to fill its valance shell.

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

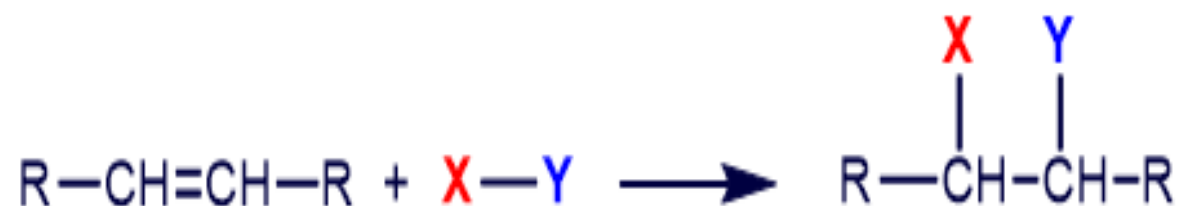
Explanation of important chemical reactions in aliphatic compounds and Identification of the functional groups.

2&3



Types of Organic Reactions

- An **addition reaction** occurs when an unsaturated reactant becomes a saturated product:



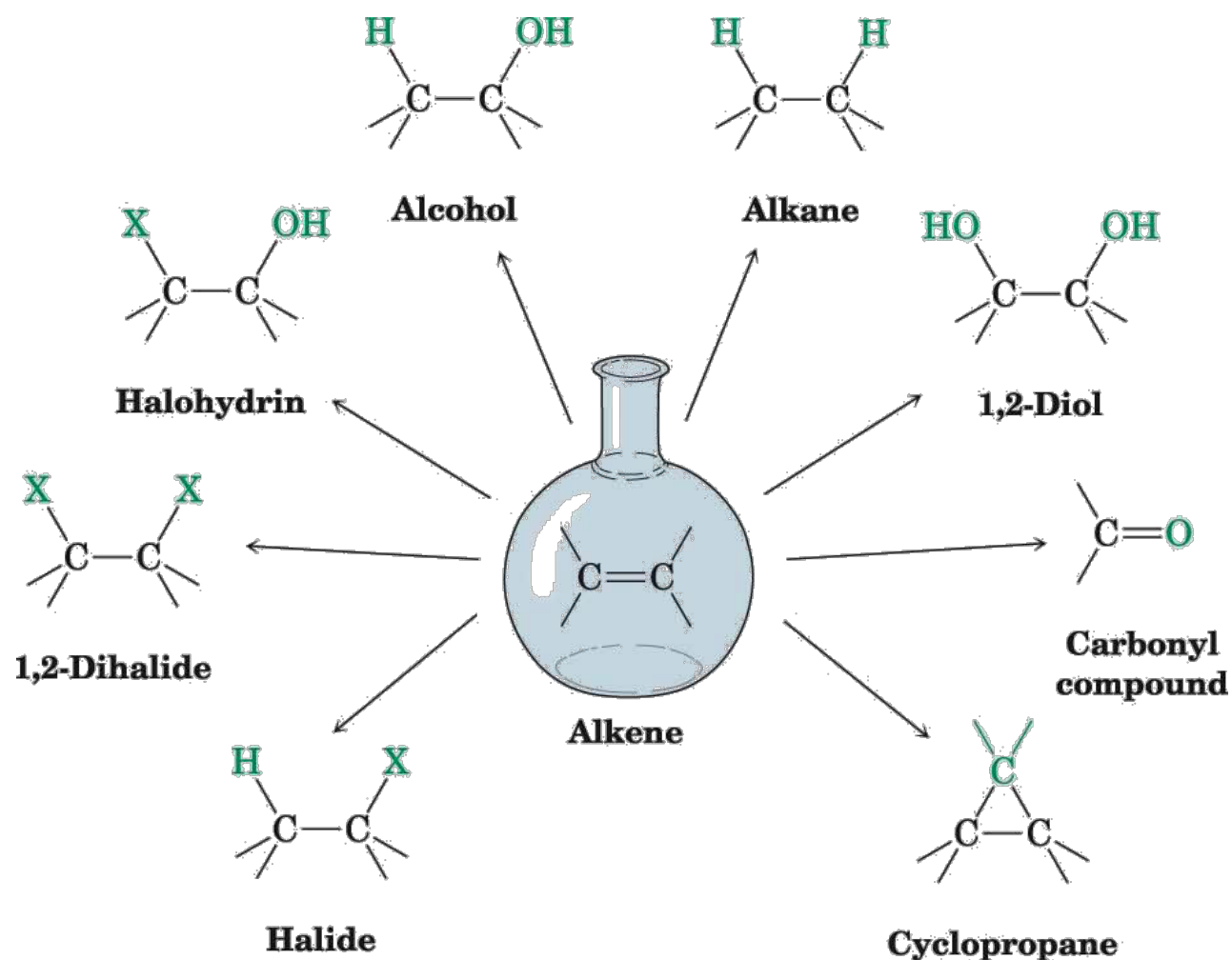
The C=C, C≡C, and C=O bonds commonly undergo addition reactions.

In each case, it is the π bond that breaks, leaving the σ bond intact.



Types of Organic Reactions

➤ An addition reaction:



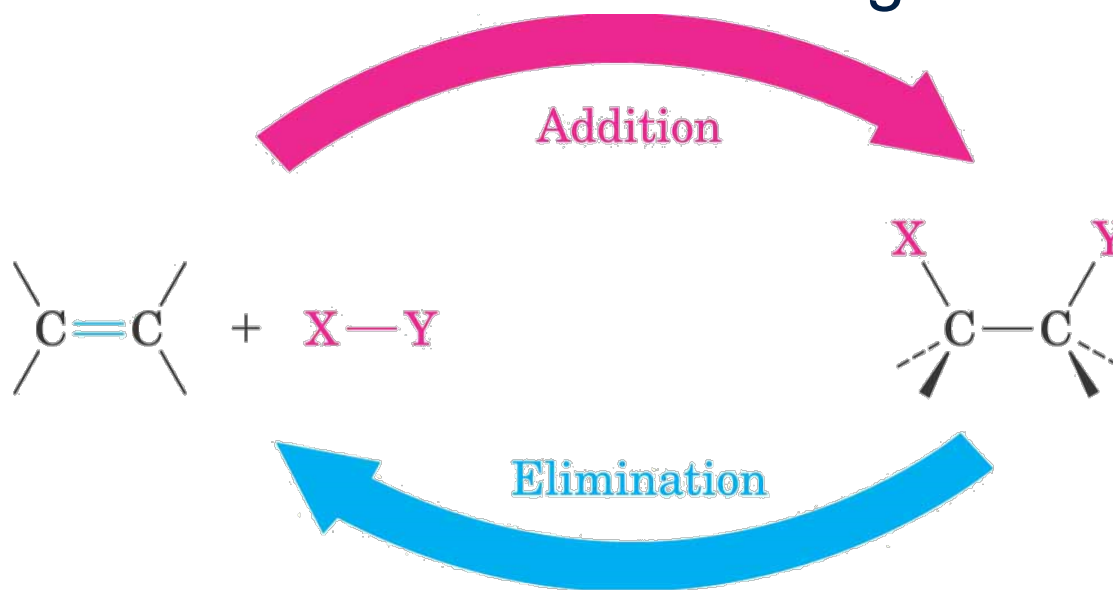


Types of Organic Reactions

- An **elimination reaction** occurs when a saturated reactant becomes an unsaturated product.
- This reaction is the reverse of addition.



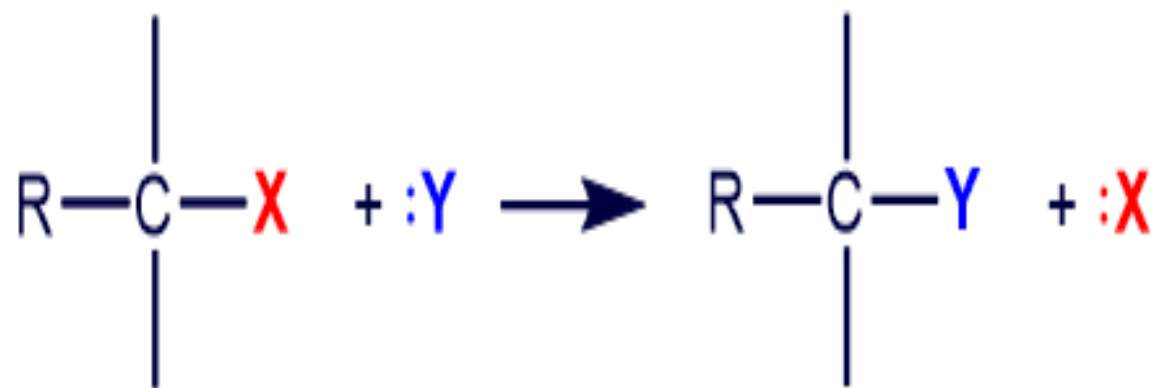
The groups typically eliminated are H and a halogen atom or H and an –OH group.





Types of Organic Reactions

- A **substitution reaction** occurs when an atom or group from an added reagent substitutes for one attached to a carbon in the organic reagent.



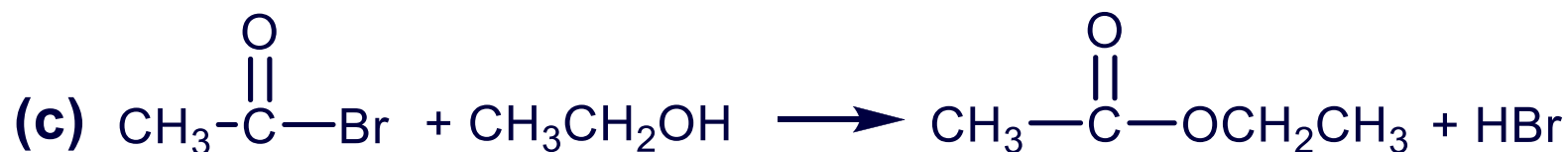
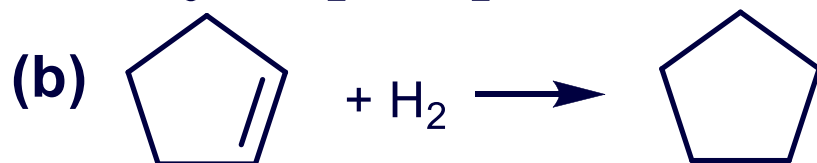
The C atom at which substitution may be saturated or unsaturated, and X and Y can be many different atoms.



Types of Organic Reactions

❖ Recognizing the Type of Organic Reaction

❖ **PROBLEM:** State whether each reaction is an addition, elimination, or substitution:



PLAN:

- We determine the type of reaction by looking for any change in the number of atoms bonded to C.
- An *addition* reaction results in more atoms bonded to C.
- An *elimination* reaction results in fewer atoms bonded to C.
- If there are the same number of atoms bonded to C, the reaction is a *substitution*.

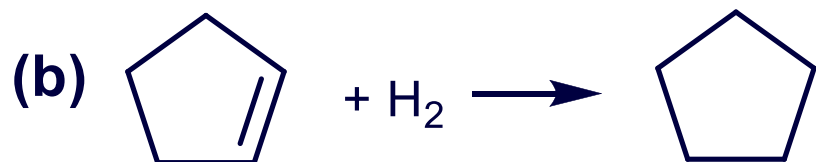


Types of Organic Reactions

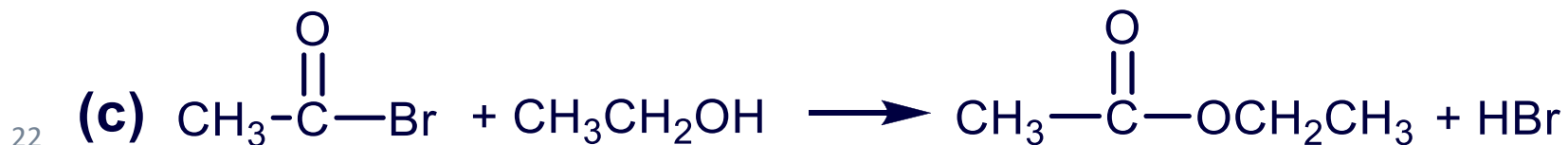
SOLUTION:



This is an **elimination** reaction; two bonds in the reactant, C—H and C—Br, are absent in the product.



This is an **addition** reaction; two more C—H bonds have formed in the product.

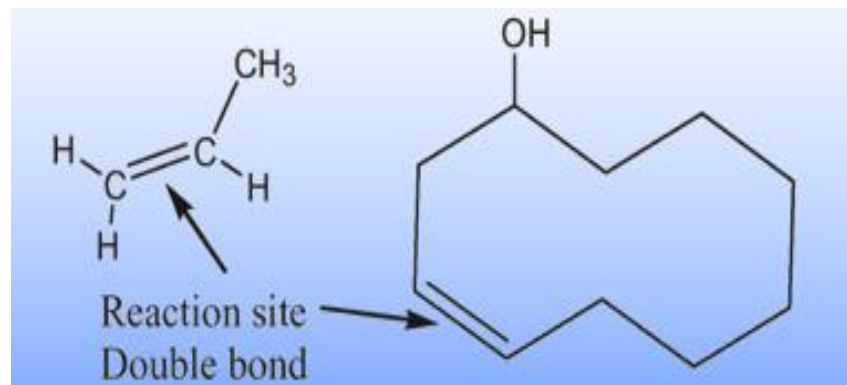


This is a **substitution** reaction; the reactant C—Br bond has been replaced by a C—O bond in the product.

Functional Groups

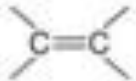
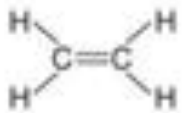
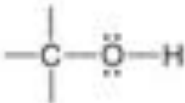
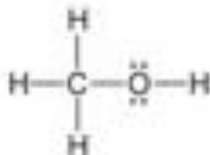
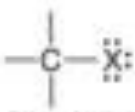
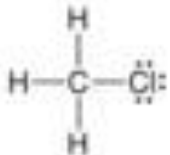
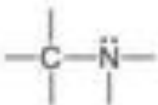
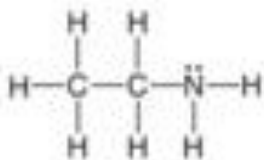
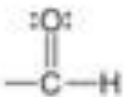
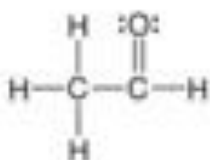
- Organic compounds are classified according to their **functional groups**.
- Functional Group** collection of atoms at a site within a molecule with a common bonding pattern.
- The functional groups in a compound **determine both its physical properties and its chemical reactivity**.
- Functional groups define the regions of high and low electron density in a compound, thus determining its reactivity.
- The group reacts in **a typical way**, generally **independent of the rest** of the molecule

For example, the double bonds in simple and complex alkenes react with bromine in the same way.

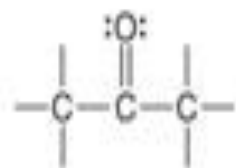


Functional Groups

Important Functional Groups in Organic Compounds:

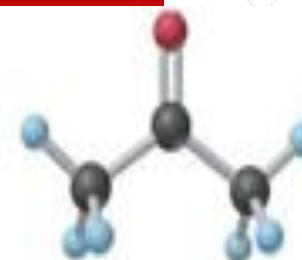
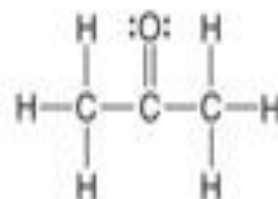
Functional Group	Compound Type	Prefix or Suffix of Name	Example		
			Lewis Structure	Ball-and-Stick Model	Systematic Name (Common Name)
	alkene	-ene			ethene (ethylene)
	alkyne	-yne			ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
 (X = halogen)	haloalkane	halo-			chloromethane (methyl chloride)
	amine	-amine			ethanamine (ethylamine)
	aldehyde	-al			ethanal (acetaldehyde)

Functional Groups

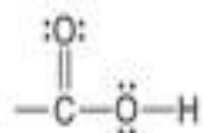


ketone

-one

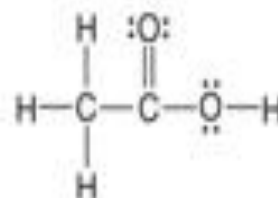


2-propanone
(acetone)

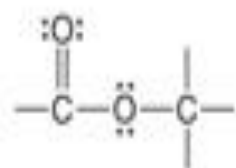


carboxylic
acid

-oic acid

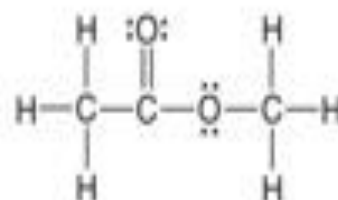


ethanoic acid
(acetic acid)

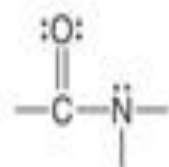


ester

-oate

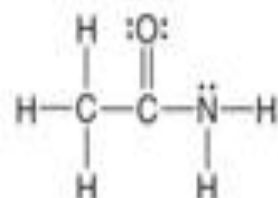


methyl ethanoate
(methyl acetate)

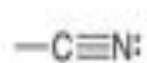


amide

-amide

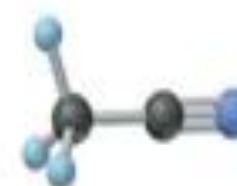
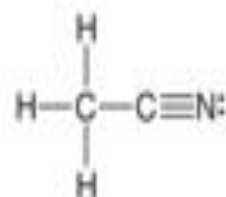


ethanamide
(acetamide)



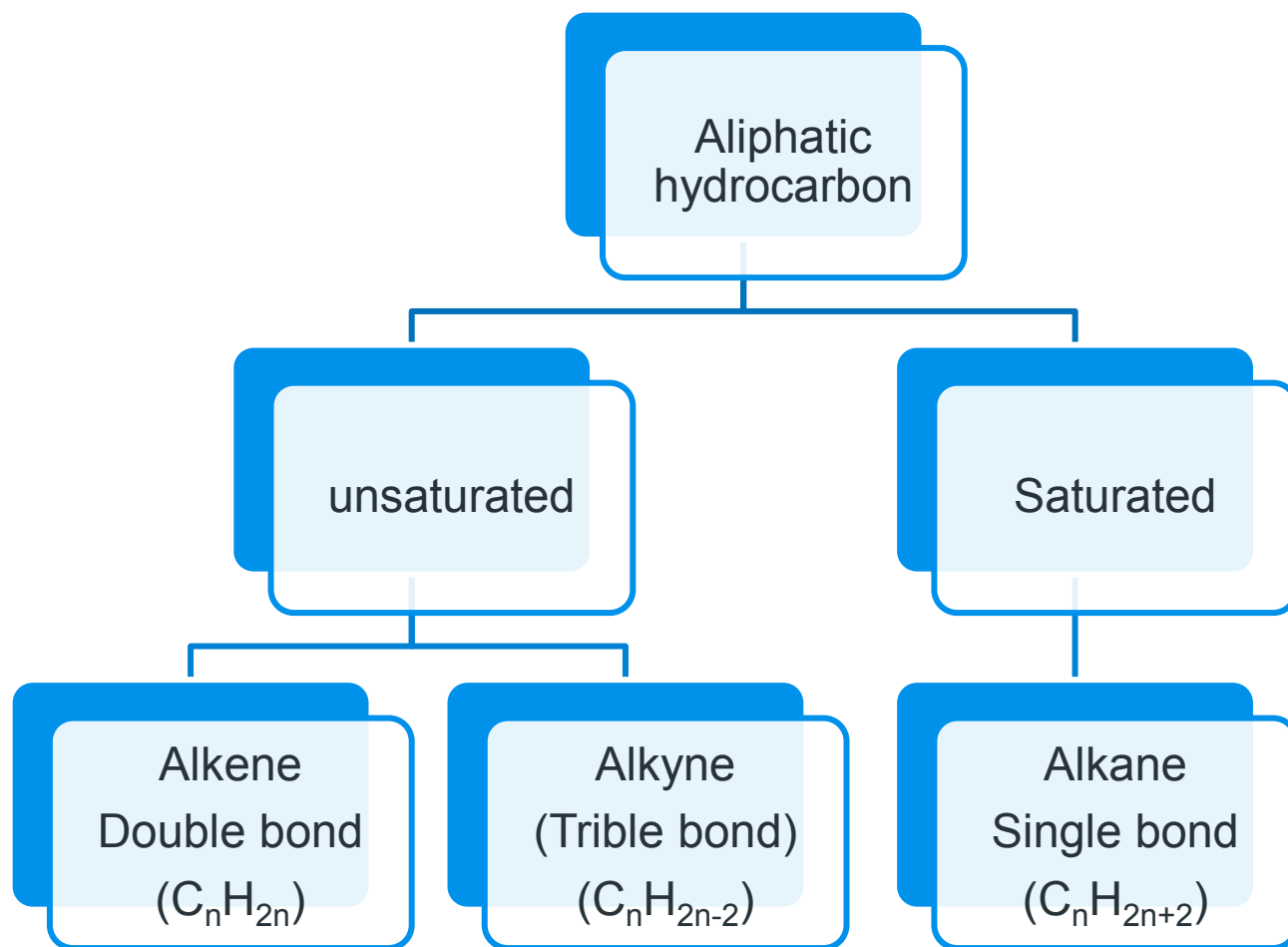
nitrile

-nitrile



ethanenitrile
(acetonitrile,
methyl cyanide)

Aliphatic Hydrocarbons



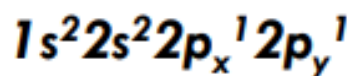
Hydrocarbons

- **Hydrocarbons** organic compounds contain of C and H
- **1. Alkanes** are hydrocarbons that contain only single bonds and are referred to as **saturated hydrocarbons**.
- Called **paraffins** (low affinity compounds) because they do not react as most chemicals
- The general formula for an alkane is C_nH_{2n+2} , where n is any positive integer.
- Alkanes comprise a **homologous series**, a group of compounds in which each member differs from the next by a $-CH_2-$ group.

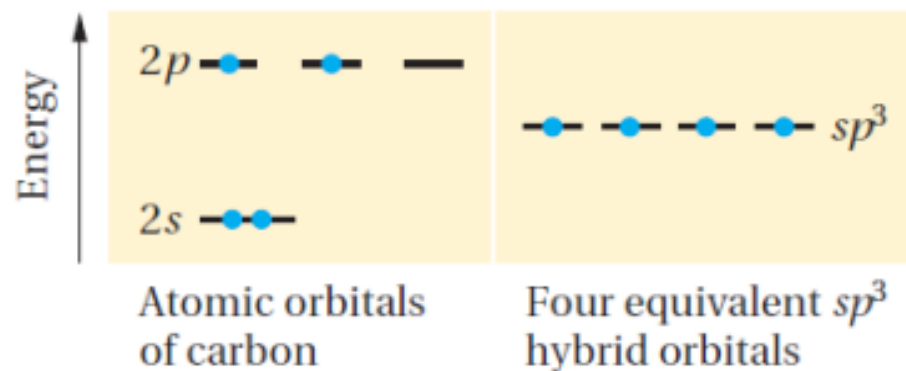
Hydrocarbons

➤ Hybridization (Alkanes sp^3):

- The electronic configuration of the isolated or ground-state carbon



Equivalent to $:\dot{\text{C}}\cdot$

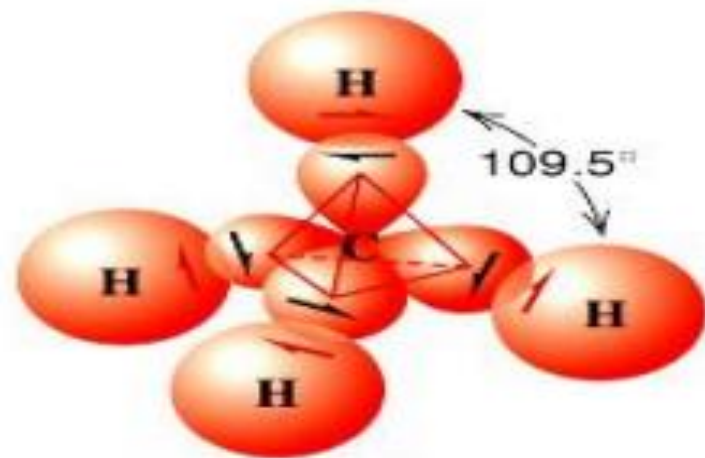
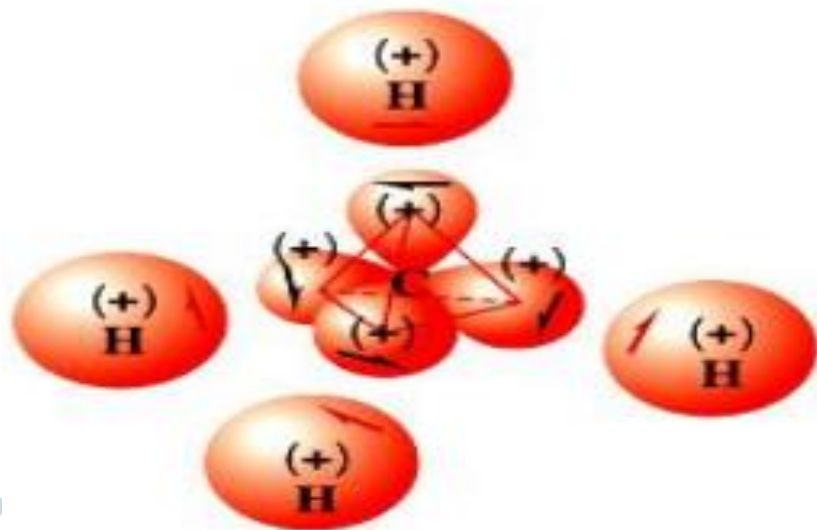
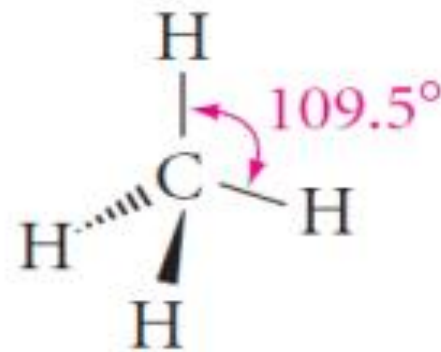
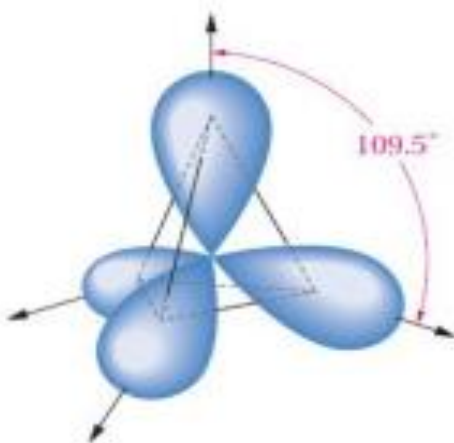


- Mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron.
- In this model, the hybrid orbitals are called **sp^3 hybrid orbitals** because each one has one part s character and three parts p character.
- Each sp^3 orbital has the same energy: less than that of the 2p orbitals but greater than that of the 2s orbital.

Hydrocarbons

➤ Hybridization (Alkanes sp^3):

- Regular tetrahedron with all H-C-H bond angles of 109.5° .



Methane, CH_4

Naming Organic Compounds

- The name of any organic compound is comprised of three portions: **PREFIX + ROOT + SUFFIX**
- The **root** name of the compound is determined from the number of C atoms in the **longest continuous chain**.
- The **suffix** indicates the **type** of organic compound and is placed after the root.
- The **prefix** identifies any groups **attached** to the main chain.

Naming Organic Compounds

❖ Names of small hydrocarbons

No. of Carbons	Formula Name	(C_nH_{2n+2})
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}
7	Heptane	C_7H_{16}
8	Octane	C_8H_{18}
9	Nonane	C_9H_{20}
10	Decane	$C_{10}H_{22}$

Naming Organic Compounds

❖ Names of larger hydrocarbons

No. of Carbons	Formula Name	(C_nH_{2n+2})
11	Undecane	$C_{12}H_{26}$
12	Dodecane	$C_{12}H_{26}$
13	Tridecane	$C_{13}H_{28}$
14	Tetradecane	$C_{14}H_{30}$
15	Pentadecane	$C_{15}H_{32}$
16	Hexadecane	$C_{16}H_{34}$
17	Heptadecane	$C_{17}H_{36}$
18	Octadecane	$C_{18}H_{38}$
19	Nonadecane	$C_{19}H_{40}$
20	Isocane	$C_{20}H_{42}$

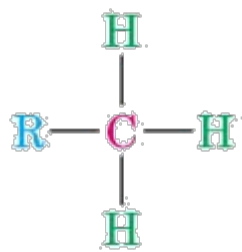
Naming Organic Compounds

❖ Alkyl group

- remove one H from an alkane (a part of a structure)
- General abbreviation “R” (for Radical, an incomplete species or the “rest” of the molecule)
- Name: replace *-ane* ending of alkane with *-yl* ending
 - CH₃ is “methyl” (from methane)
 - CH₂CH₃ is “ethyl” (from ethane)

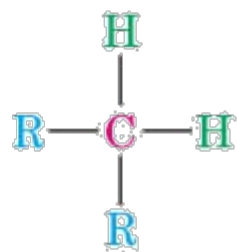
❖ Types of Alkyl groups

- a carbon at the end of a chain (primary alkyl group)
- a carbon in the middle of a chain (secondary alkyl group)
- a carbon with three carbons attached to it (tertiary alkyl group)

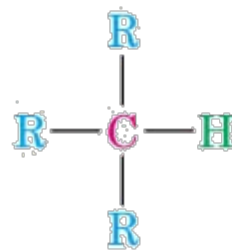


Primary carbon (1^o)
is bonded to one
other carbon

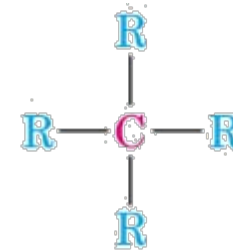
© Thomson - Brooks Cole



Secondary carbon (2^o)
is bonded to two
other carbons



Tertiary carbon (3^o)
is bonded to three
other carbons



Quaternary carbon (4^o)
is bonded to four
other carbons

Naming Organic Compounds

○ Numerical **Roots** for Carbon Chains and Branches

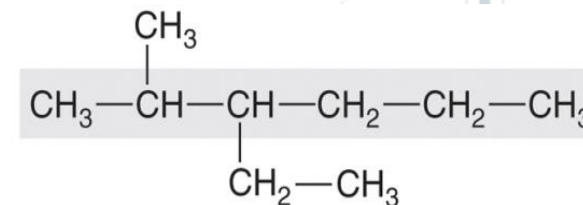
Roots	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
<u>hept-</u>	7
<u>oct-</u>	8
non-	9
<u>dec-</u>	10

Naming Organic Compounds

Rules for Naming an Organic Compound

1. Naming the longest chain (root)

- Find the longest *continuous* chain of C atoms.
- Select the root that corresponds to the number of C atoms in this chain.



6 carbons $\Rightarrow$ hex-

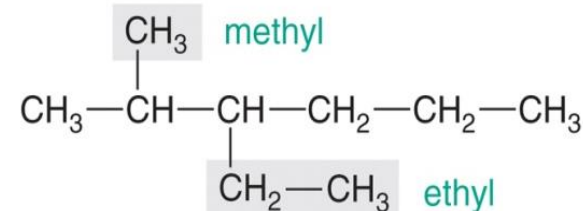
2. Naming the compound type (suffix)

- For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
- If the chain forms a ring, the name is preceded by *cyclo-*.

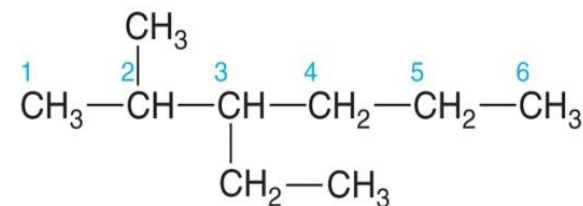
hex- + *-ane* $\Rightarrow$ hexane

3. Naming the branches (prefixes) (If the compound has no branches, the name consists of the root and suffix.)

- Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
- Branch names precede the chain name. When two or more branches are present, their names appear in *alphabetical* order.
- To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the main-chain C to which that branch is attached.



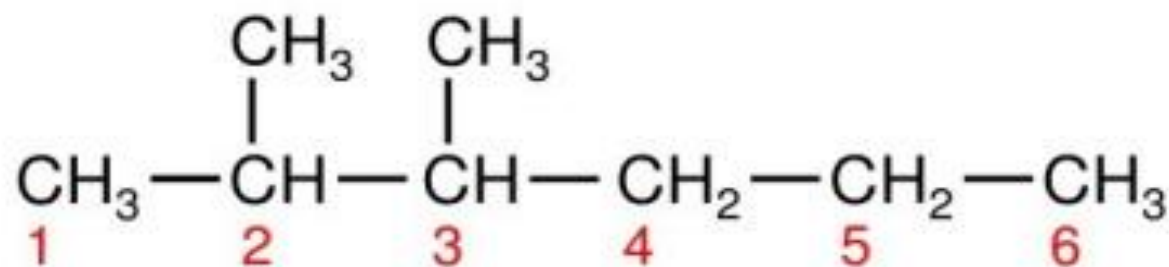
ethylmethylhexane



3-ethyl-2-methylhexane

Naming Organic Compounds

4. Use prefixes *di-*, *tri-*, *tetra-*, when there is more than one alkyl branch of the same kind.



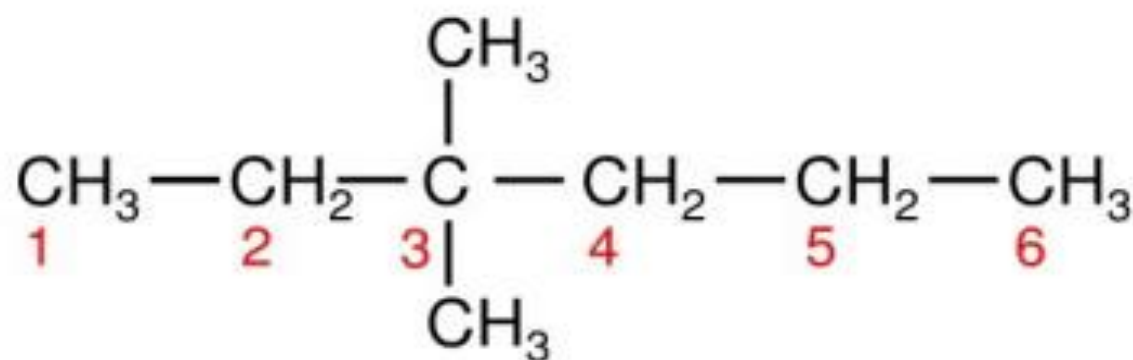
2,3-**di**methylhexane

Prefixes:

di means double

tri means triple

tetra means quadruple

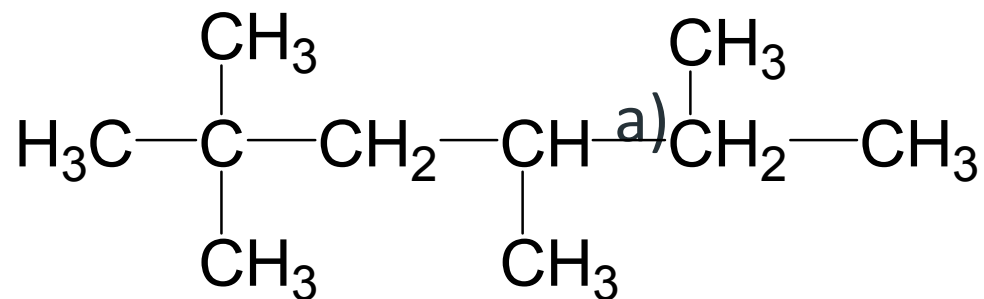


3,3-**di**methylhexane

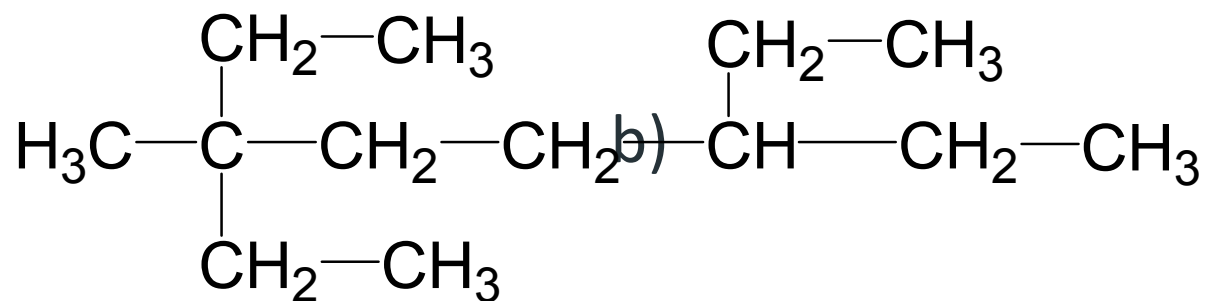
Naming Organic Compounds

EXERCISE!

NAME EACH OF THE FOLLOWING:



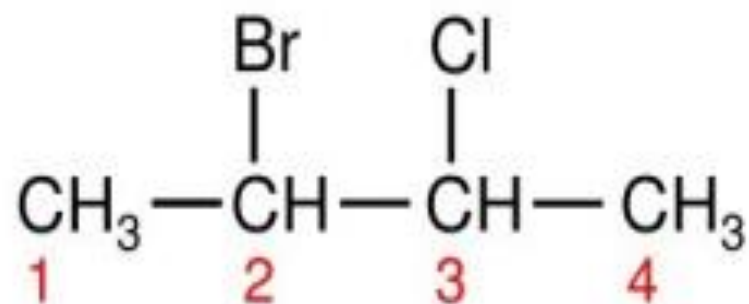
2,2,4,5-tetramethylhexane



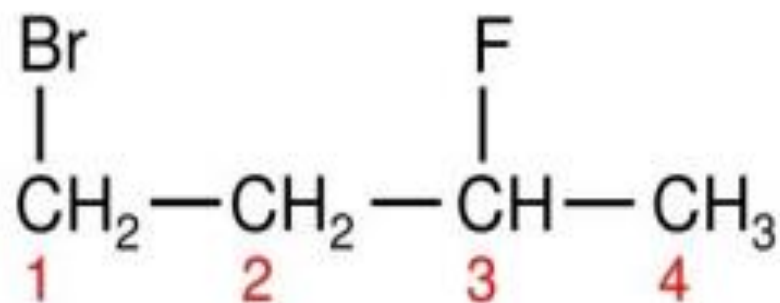
3,6-diethyl-3-methyloctane

Naming Organic Compounds

5. Use previous rules for other types of **substituents**.



2-bromo-3-chlorobutane



1-bromo-3-fluorobutane

Names of Common Substituent Groups

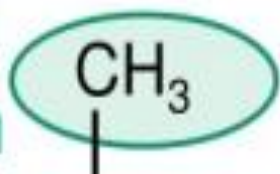
<u>Functional Group</u>	<u>Name</u>
-F	fluoro
-Cl	chloro
-Br	bromo
-I	iodo
-NO ₂	nitro

Naming Organic Compounds

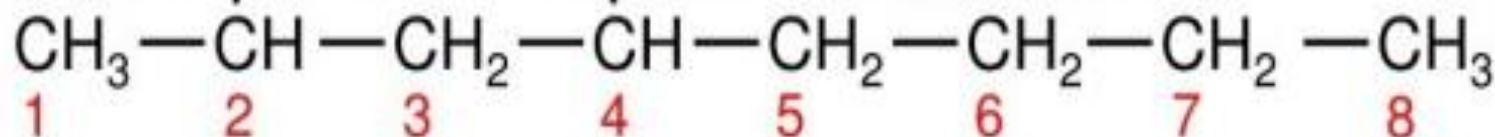
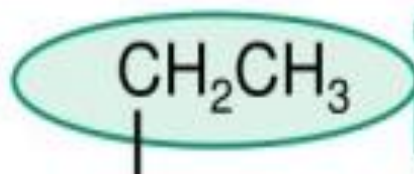


What is the IUPAC name of the following compound?

methyl
branch



ethyl
branch



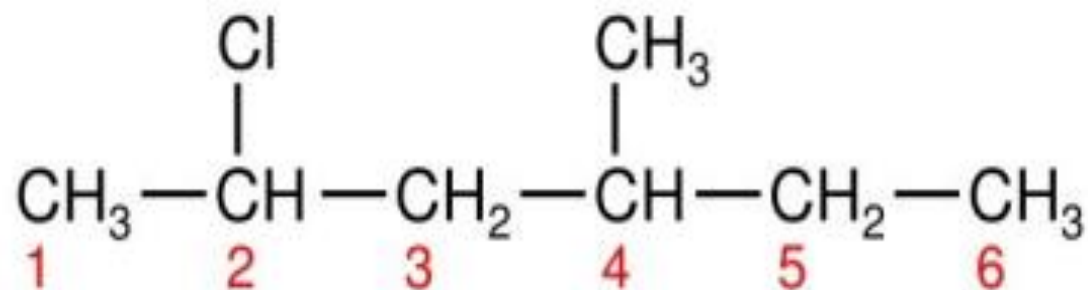
...octane

4-ethyl-2-methyloctane

Yes, the groups (branches) need to be listed alphabetical!



What is the structure of 2-chloro-4-methylhexane?



Constitutional Isomers

- **Constitutional or structural isomers** have the same **molecular formula** but a different **arrangement** of the bonded atoms.
- A straight-chain alkane may have many branched structural isomers.
- Structural isomers are different compounds and have different properties.
- If the isomers contain the same functional groups, their properties will still be similar.

The Constitutional Isomers of C_5H_{12}

The isomer for C4-C7 Can be calculate by $2^{n-4}+1$.

C8 by $2^{n-4}+2$

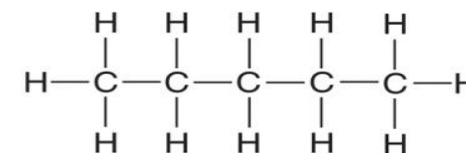
Exa:

How many isomer for C_5H_{12} ?

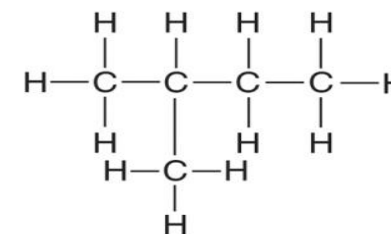
Ans:

$$2^{n-4}+1 = 2^{5-4}+1 = 3$$

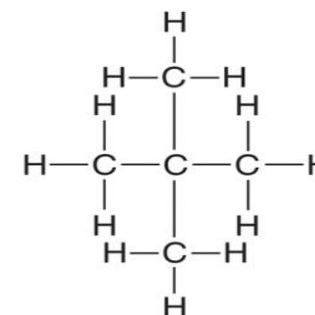
Pentane
(*n*-pentane)



2-Methylbutane
(isopentane)



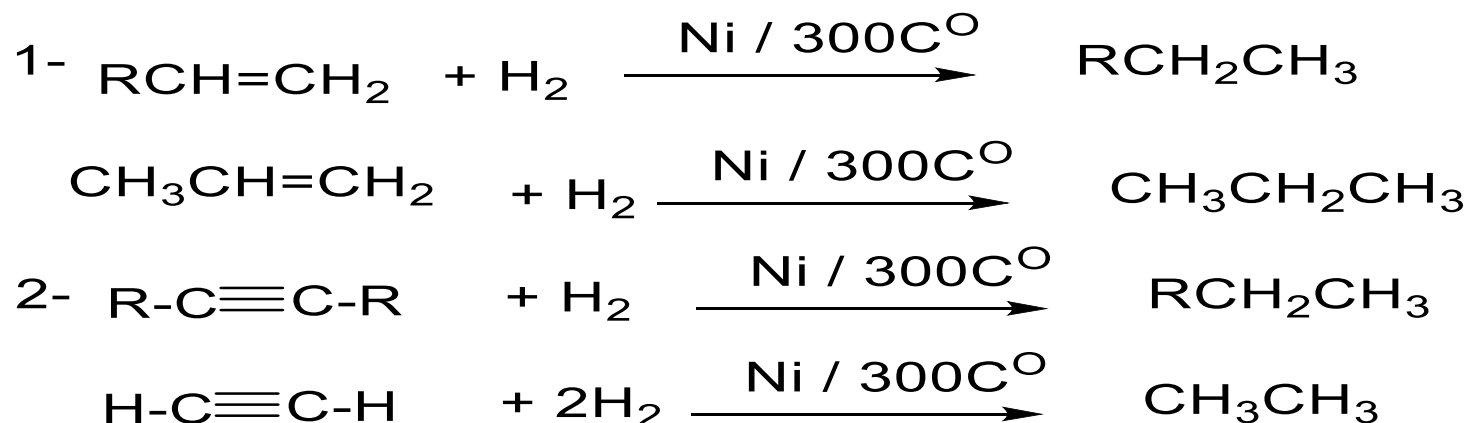
2,2-Dimethylpropane
(neopentane)



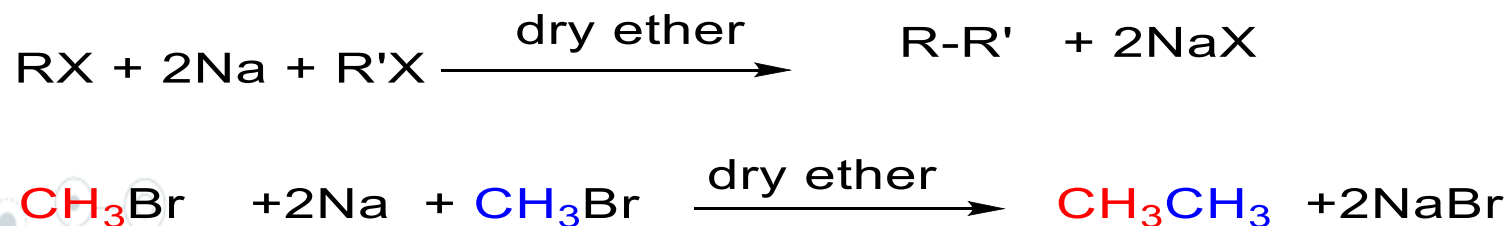
PREPERATION OF ALKANE

○ Sabtier and senderns reaction)

BY hydrogenation of unsaturated hydrocarbon in presence of Ni at high temperature(200-300C^o).

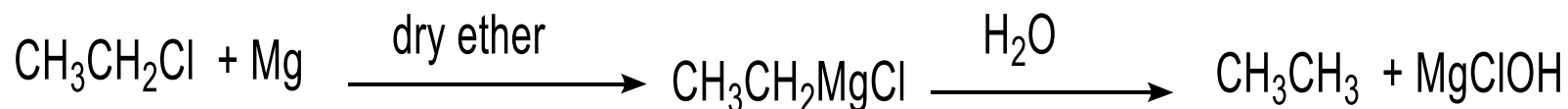
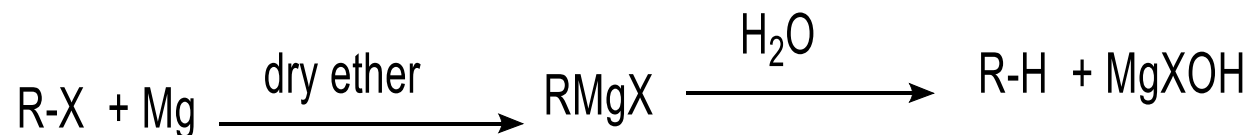


2- Wurtz reaction :reaction of Na with alkyl halide to give alkane



PREPERATION OF ALKANE

○ 3-hydrolysis of Grignard reaction



Physical properties:

a- C1-C4 are gas

b- C5-C17 are liquids

C- C18 are waxy solid

D- nonpolar molecules and hence are insoluble in water

but dissolve in organic solvents such as benzene and carbon tetrachloride

E- boiling points of alkanes increase with increase molecular weight

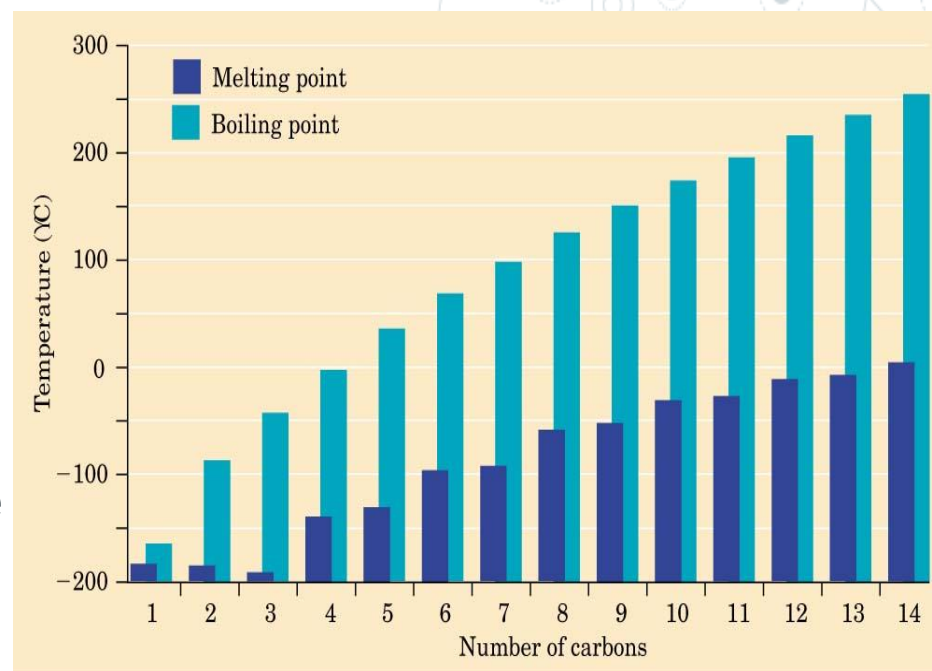
f- the branched chain alkane will have a lower boiling point than the corresponding n-isomer

G- all alkanes have densities less than 1.0 g/mL and are therefore less dense than water

Hydrocarbons

➤ 1. Alkanes:

- Alkanes are **nonpolar** and their physical properties are determined by the ***dispersion forces*** between their molecules.
- Forces between molecules (temporary dipoles, dispersion) are weak



© Thomson - Brooks Cole

- They react with Cl_2 in the presence of light to replace H's with Cl's (not controlled)

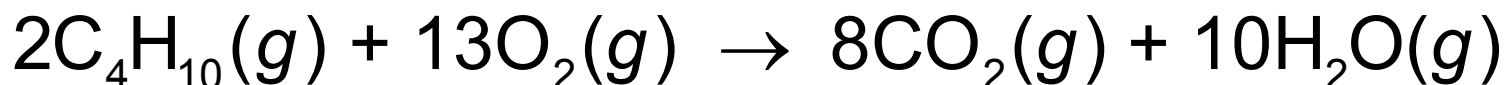


Reactions of Alkanes

❖ (oxidation)

Combustion Reactions of Alkanes

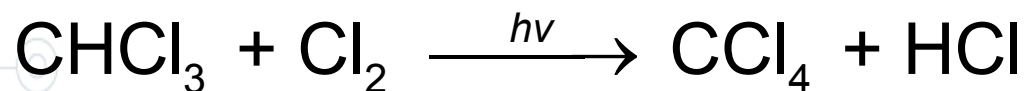
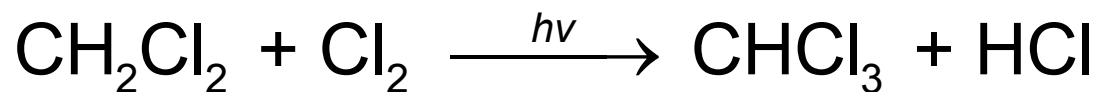
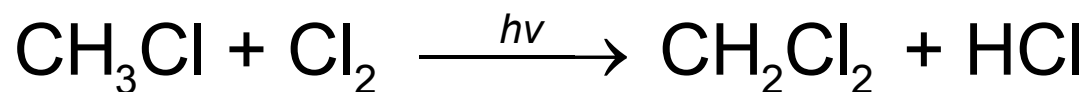
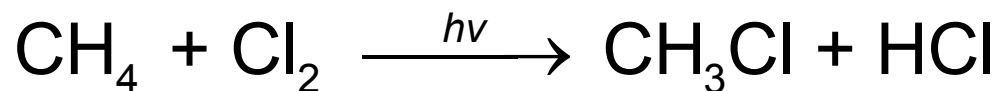
- At a high temperature, alkanes react vigorously and exothermically with oxygen.
- Basis for use as fuels.



❖ Substitution Reactions of Alkanes

1-(halogenation)

- Primarily where halogen atoms replace hydrogen atoms.



The reactivity of alkane in substituted is $3^\circ > 2^\circ > 1^\circ$

Reactions of Alkanes

2- Nitration :

When a mixture of an alkane and HNO_3 at $400\text{--}500^\circ\text{C}$, ONE hydrogen in alkane is substituted by nitro group



Nitroethane

❖ (ELEMENATION)

Dehydrogenation Reactions of Alkanes

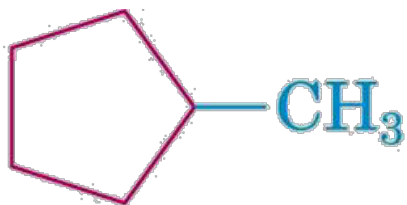
- Hydrogen atoms are removed and the product is an unsaturated hydrocarbon.



cycloHydrocarbons

➤ Naming Cycloalkanes

- Count the number of carbon atoms in the ring and the number in the largest substituent chain. If the number of carbon atoms in the ring is equal to or greater than the number in the substituent, the compound is named as an alkyl-substituted cycloalkane
- For an alkyl- or halo-substituted cycloalkane, start at a point of attachment as C1 and number the substituents on the ring so that the *second* substituent has as low a number as possible.
- Number the substituents and write the name



BUT



Methylcyclopentane

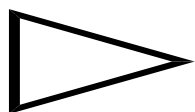
© Thomson - Brooks/Cole

1-Cyclopropylbutane

Hydrocarbons

❖ Cycloalkanes:

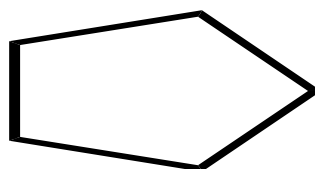
- **Cycloalkanes** are **alkanes** that have carbon atoms that form a ring (called alicyclic compounds)
- Simple cycloalkanes rings of $\text{—CH}_2\text{—}$ units, $(\text{CH}_2)_n$, or C_nH_{2n}
- Structure is shown as a regular polygon with the number of vertices equal to the number of C's (a projection of the actual structure)



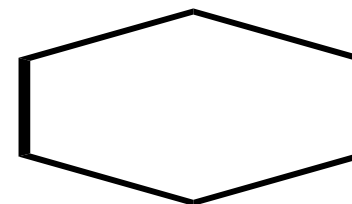
cyclopropane



cyclobutane

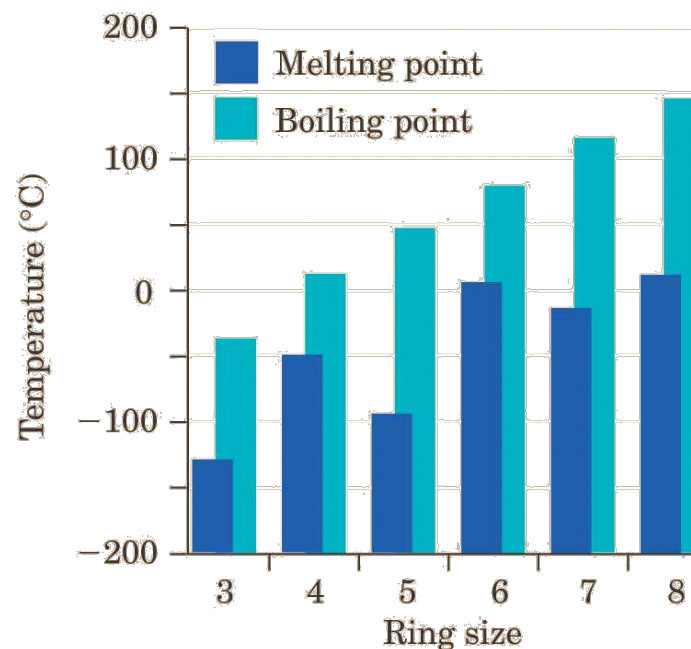


cyclopentane



cyclohexane

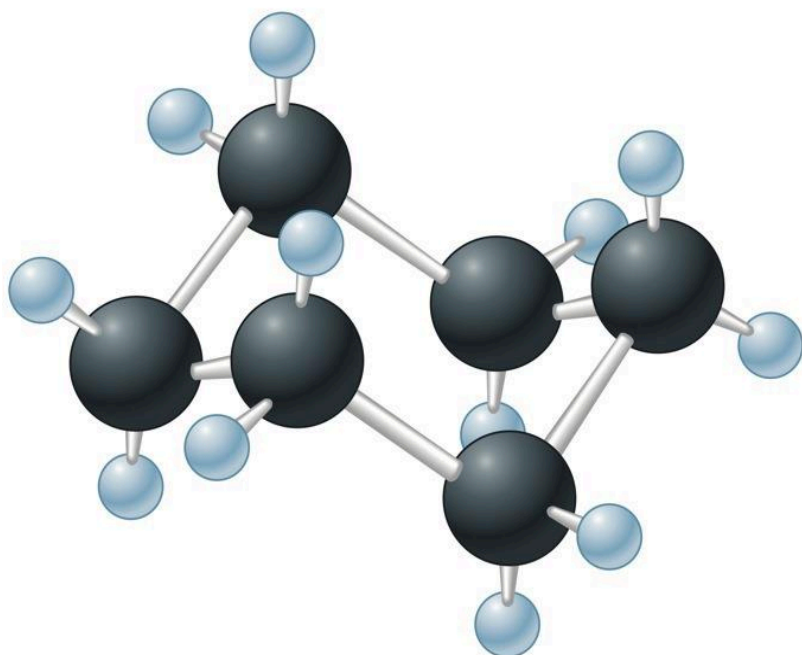
❑ Melting points are affected by the shapes and the way that crystals pack so they do not change uniformly



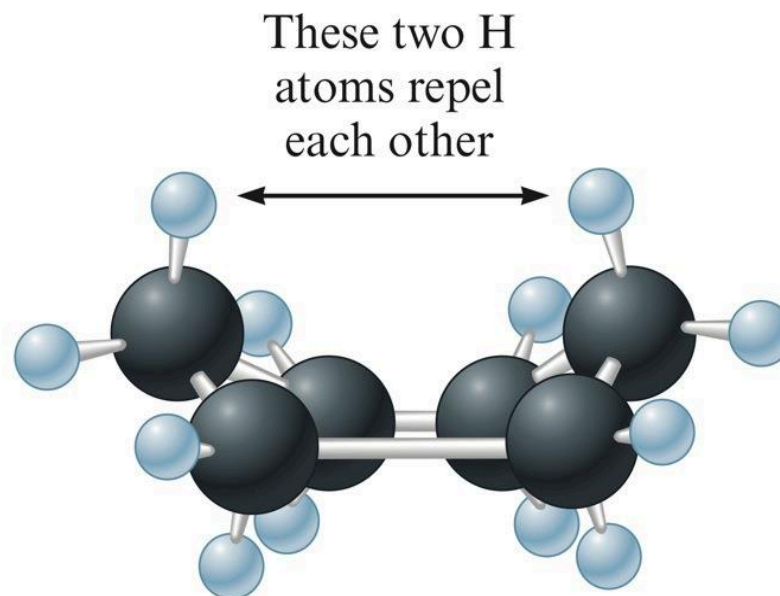
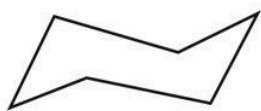
Hydrocarbons

❖ Cycloalkanes:

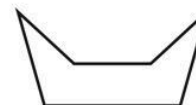
➤ The Chair and Boat Forms of Cyclohexane



Chair



Boat



a

b

Hydrocarbons

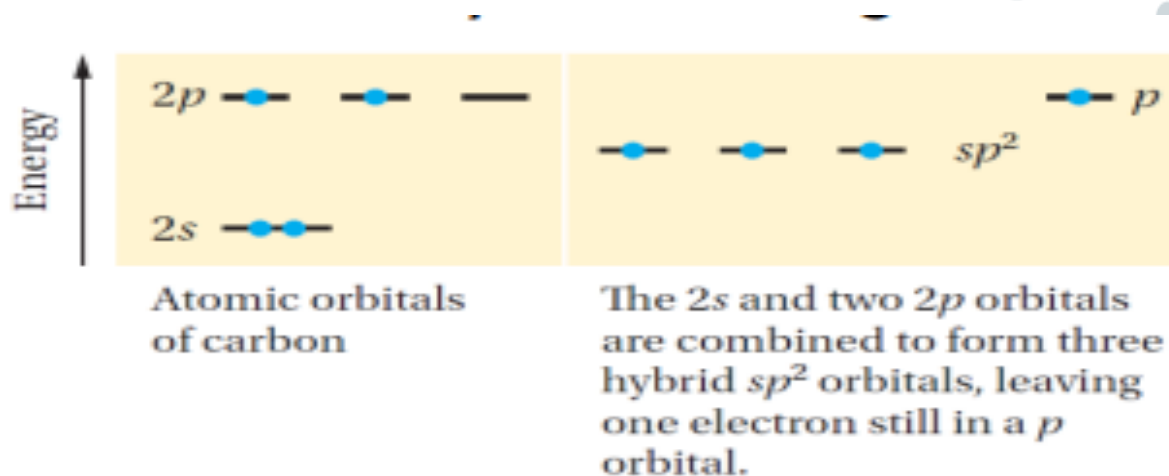
➤ 2. alkene

- Unsaturated compound that contains at least one C=C bond is called an **alkene**.
- Alkenes are **unsaturated** and have the general formula C_nH_{2n} .
- Also called an **olefin** but *alkene* is better
- To name an alkene, the **root** name is determined by the number of C atoms in the **longest chain** that also **contains the double bond**.
- The C chain is **numbered** from the end **closest** to the **double bond**.
- The **suffix** for alkenes is **–ene**.

Alkenes

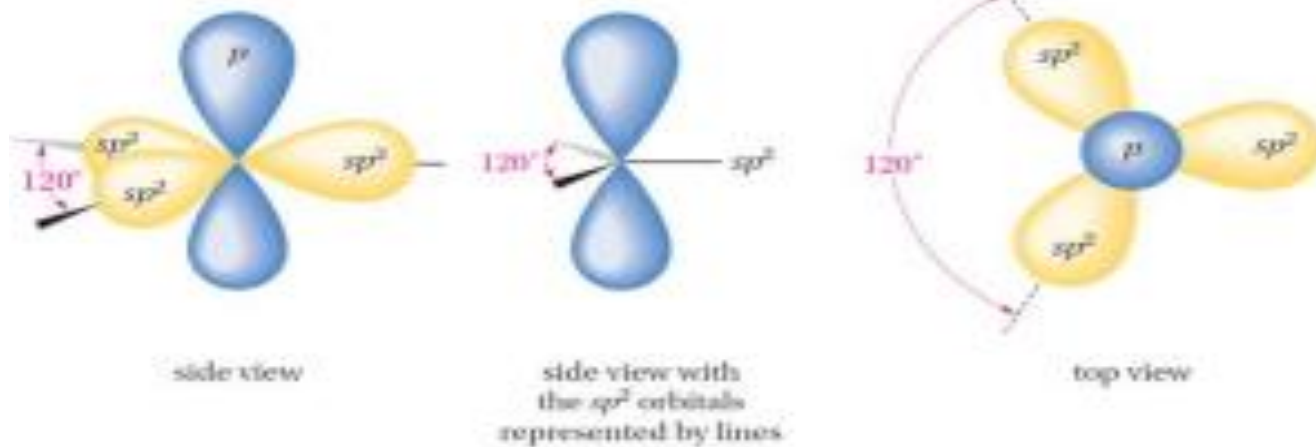
➤ Hybridization (Alkenes sp^2):

- The electronic configuration of the isolated or ground-state carbon
Combine only three of the orbitals, to make three equivalent sp^2 - **hybridized orbitals** (called sp^2 because they are formed by combining one s and two p orbitals)

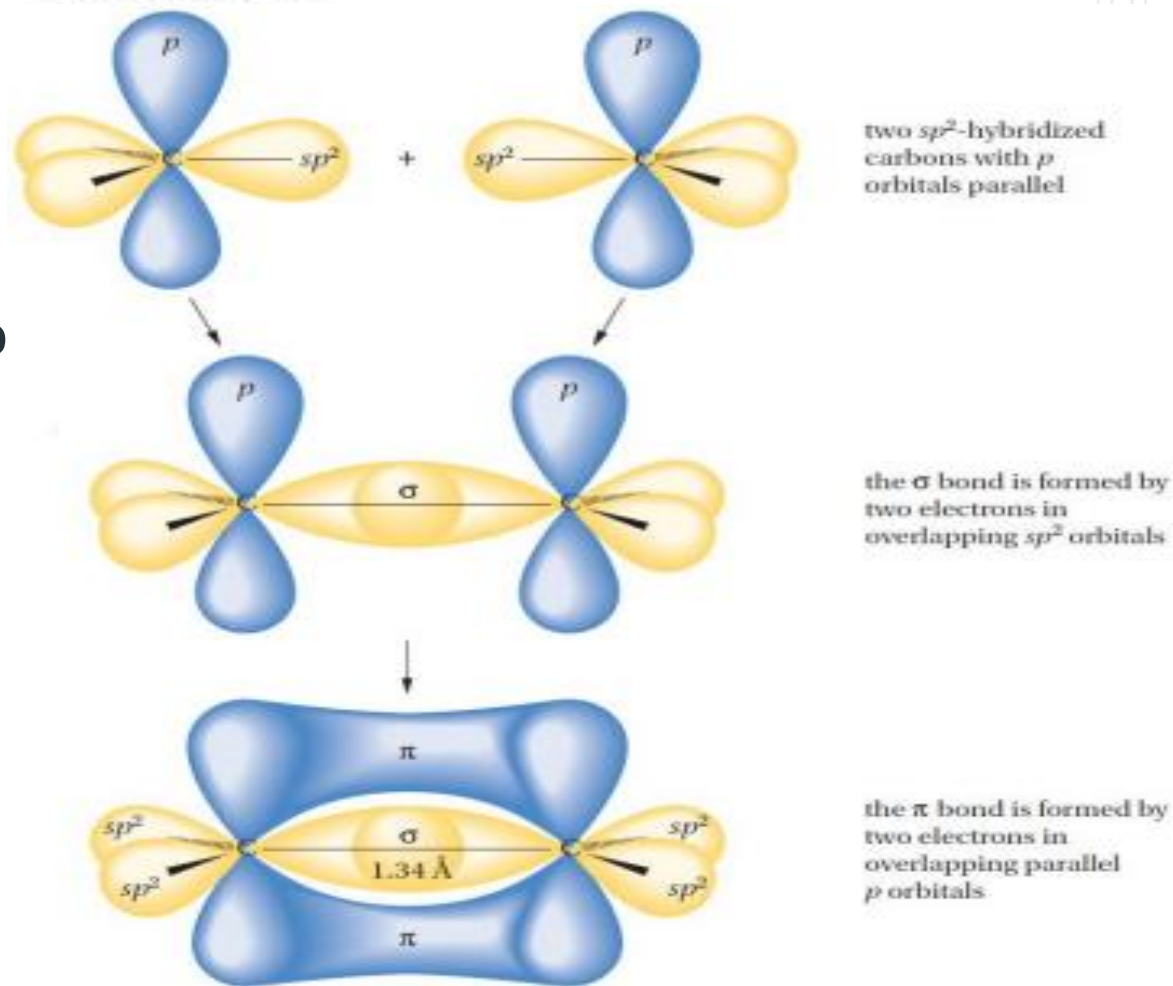


- Three valence electrons are placed in the three sp^2 orbitals. The fourth valence electron is placed in the remaining 2p orbital, whose axis is perpendicular to the plane formed by the three sp^2 hybrid orbitals.
- A trigonal carbon with bond angles of 120° .

Alkenes



- **Hybridization (Alkenes sp^2):**
 - Schematic formation of a carbon–carbon double bond. Two sp^2 carbons form a sigma (σ) bond (end-on overlap of two sp^2 orbitals) and a pi (π) bond (lateral overlap of two properly aligned p orbitals).



Naming Organic Compounds

EXERCISE!

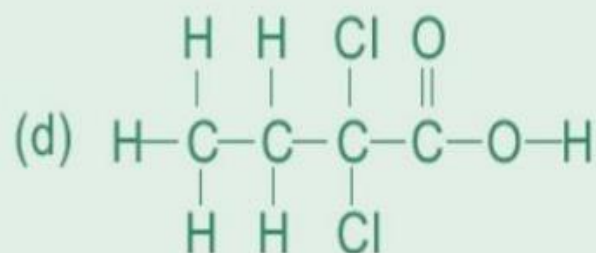
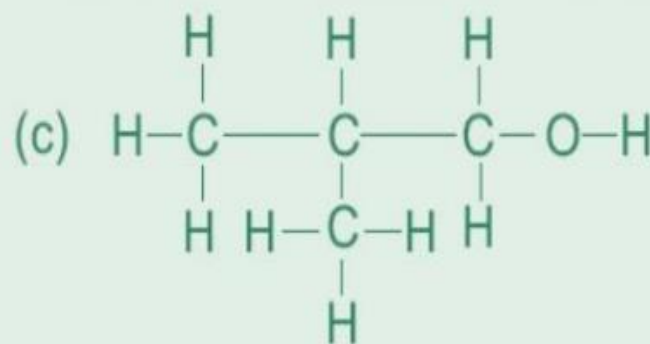
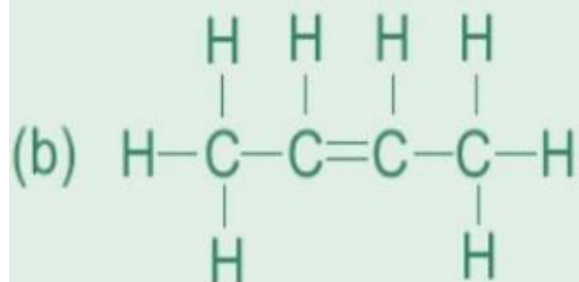
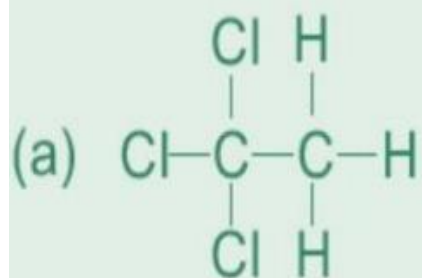
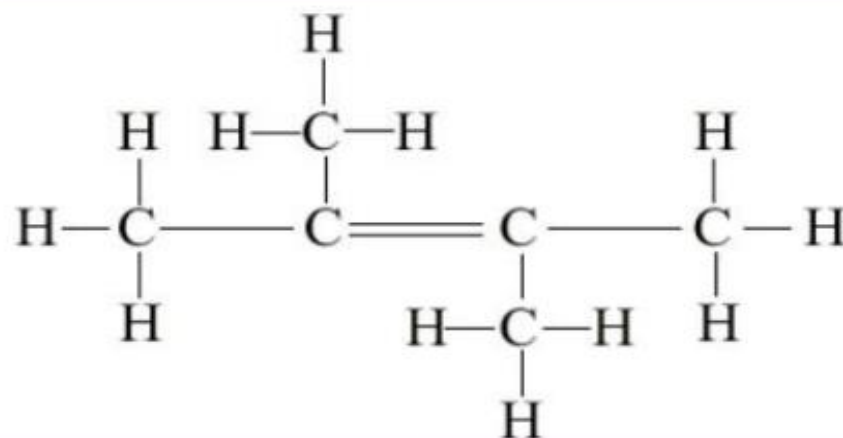
Write the structural formula for 2,3-dimethylbut-2-ene.

Solution

Steps	Example (2,3-dimethylbut-2-ene)
(1) Write the main carbon chain. (Do not add hydrogen atoms at this moment.)	$\text{C} - \text{C} - \text{C} - \text{C}$
(2) Number the main carbon chain.	${}^1\text{C} - {}^2\text{C} - {}^3\text{C} - {}^4\text{C}$
(3) In the main chain, add the substituents to correct places and put down the carbon-carbon double bond.	$\begin{array}{c} \text{C} \\ \\ {}^1\text{C} - {}^2\text{C} = {}^3\text{C} - {}^4\text{C} \\ \\ \text{C} \end{array}$

Naming Organic Compounds

- (4) Add the correct number of hydrogen atoms to complete the structural formula.
(Check that each atom has the correct number of covalent bonds attached to it.)

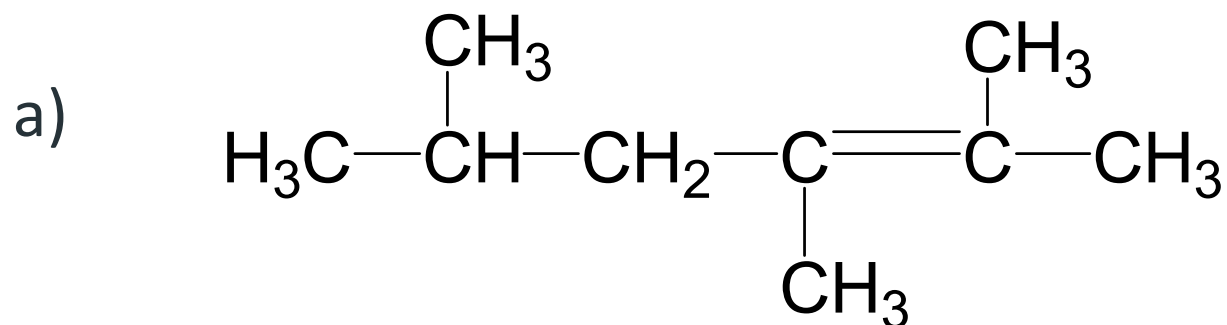


Hydrocarbons

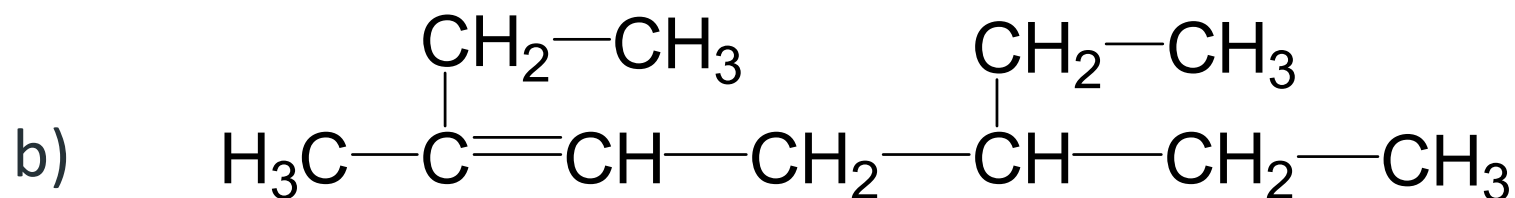
➤ 2. alkene

EXERCISE!

NAME EACH OF THE FOLLOWING:



2,3,5-trimethyl-2-hexene

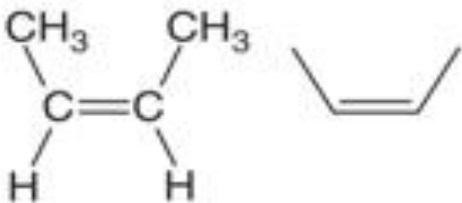
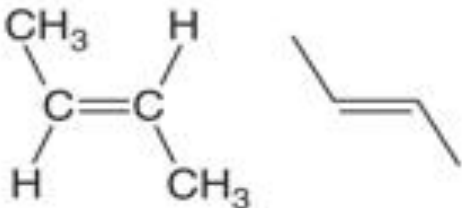


6-ethyl-3-methyl-3-octene

Geometric Isomers

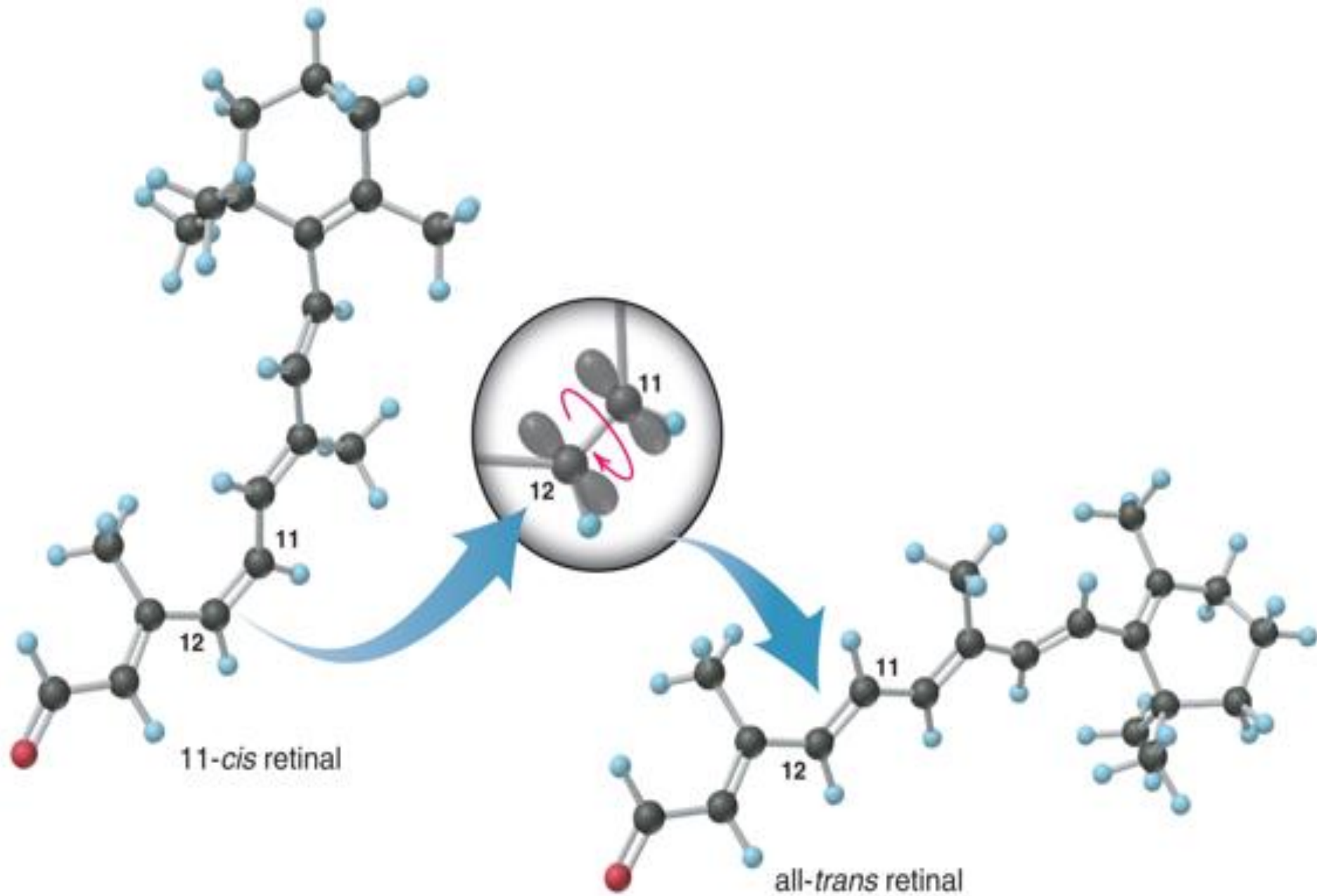
- The double bond of an alkene restricts **rotation**, so that the relative positions of the atoms attached to the double bond are fixed.
- **Alkenes** may exist as geometric or cis-trans isomers, which differ in the **orientation** of the groups attached to the **double** bond.
- Geometric isomers have **different** physical properties.

The Geometric Isomers of 2-Butene

Systematic Name	Condensed and Skeleton Formulas	Space-Filling Model	Density (g/mL)	Boiling Point (°C)
<i>cis</i> -2-Butene			0.621	3.7
<i>trans</i> -2-Butene			0.604	0.9

Geometric Isomers

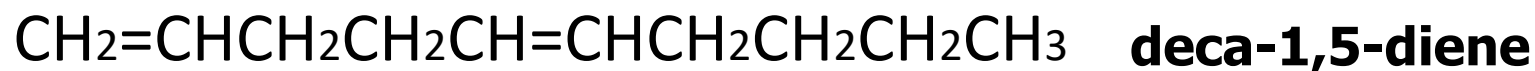
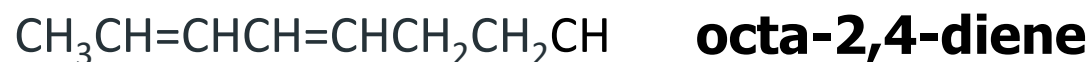
- The initial chemical event in vision and the change in the shape of retinal.



NAMING ACCORDING THE NUMBER OF DOUBLE BOND

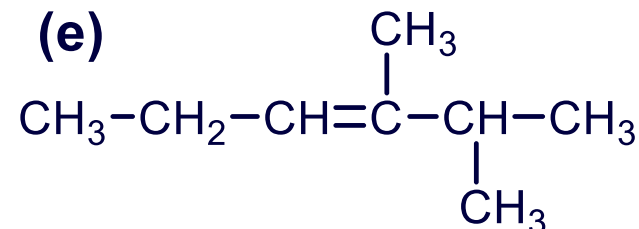
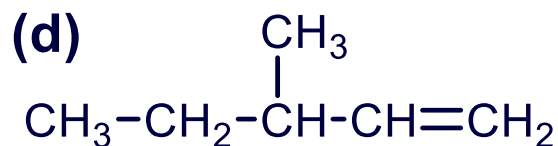
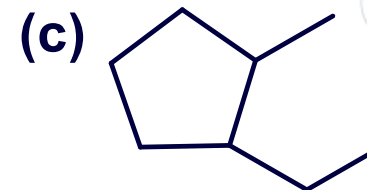
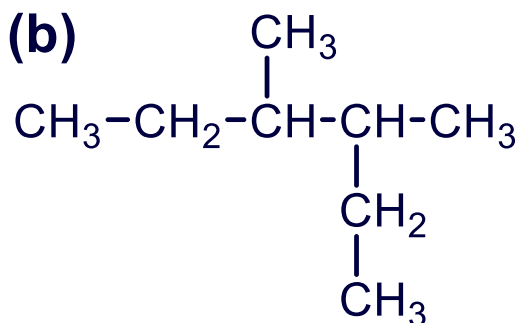
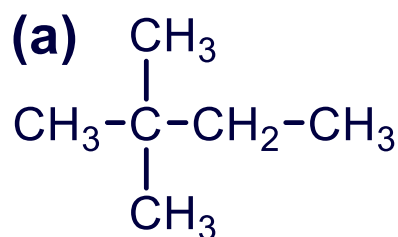
Rule

If there is more than one double bond in an alkene, all of the bonds should be numbered in the name of the molecule - even terminal double bonds. The numbers should go from lowest to highest, and be separated from one another by a comma. The IUPAC numerical prefixes are used to indicate the number of double bonds



Hydrocarbons

Sample Problem: Naming Alkanes, Alkenes, and Alkynes?

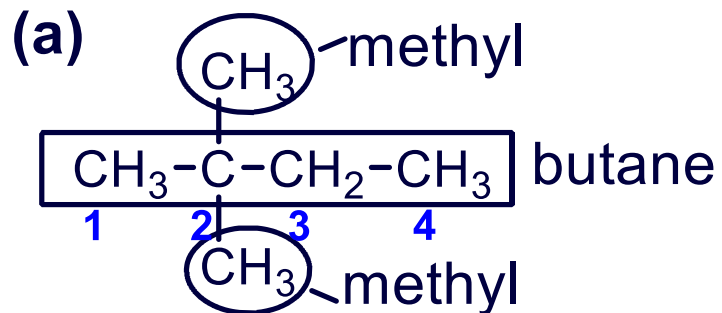


PLAN: For (a) to (c), we find the **longest** continuous chain (root) and add the suffix **-ane** because there are only **single** bonds. Then we name the branches, numbering the C chain from the end **closest to the first branch** and name the branches with the (*root + yl*).

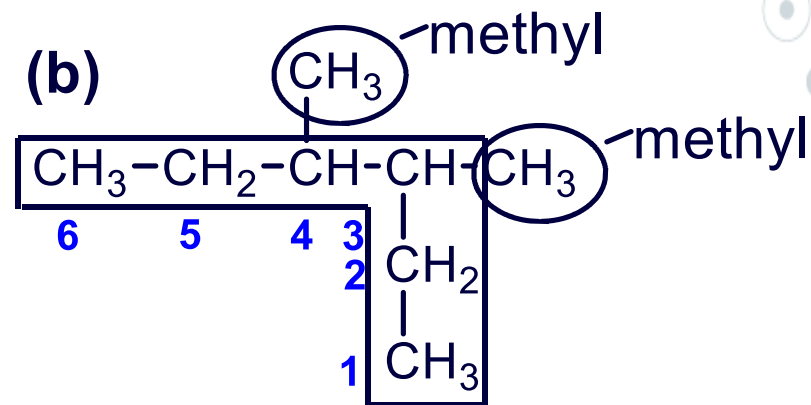
For (d) and (e) the **longest** chain must include the **double** bond and the chain must be numbered such that the double bond occurs on the lowest numbered carbo.

Hydrocarbons

SOLUTION:

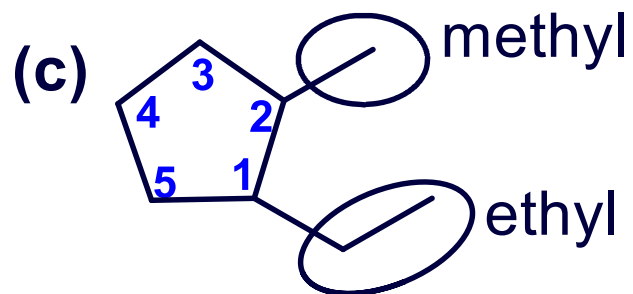


2,3-dimethylbutane



hexane

3,4-dimethylhexane



1-ethyl-2-methylcyclopentane

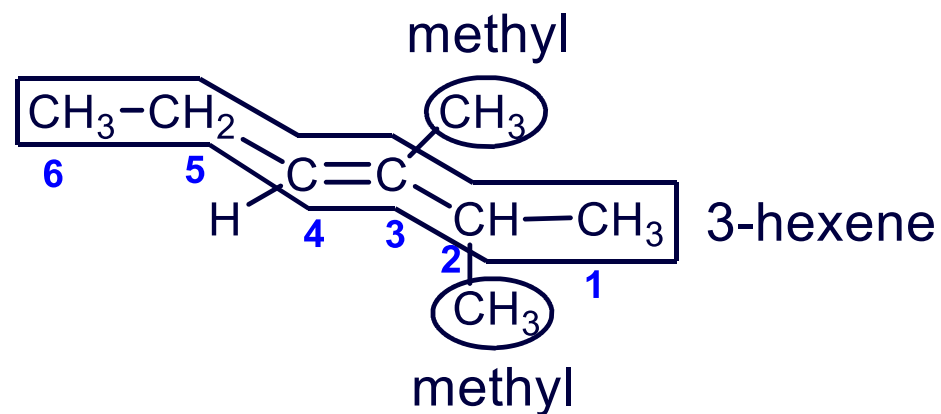
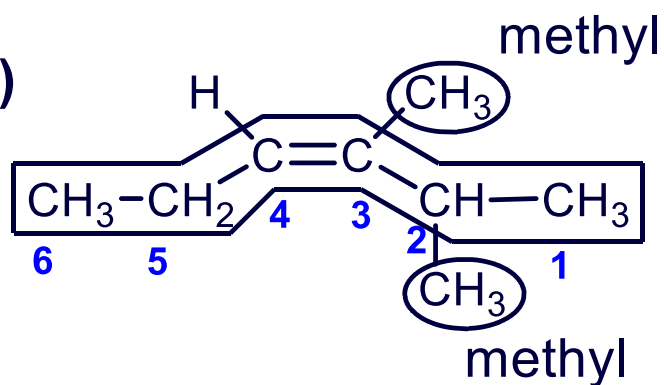
Hydrocarbons

SOLUTION:

(d)



(e)



***cis*-2,3-dimethyl-3-hexene**

PHYSICAL PROPERTIES OF ALKENE

- Alkene from C₂-C₄ are gases, C₅-C₁₅ are liquid and above the C₁₅ is solid
- Alkenes are insoluble in water but soluble in organic solvent
- Alkenes are light than water
- The melting point and boiling point rise with increase molecular weight
- Branch chain alkenes have lower boiling point than straight chain
- Alkenes have higher melting point than alkanes

Importance:

common group in biological molecules

starting material for synthesis of many plastics



PREPARATION OF ALKENE

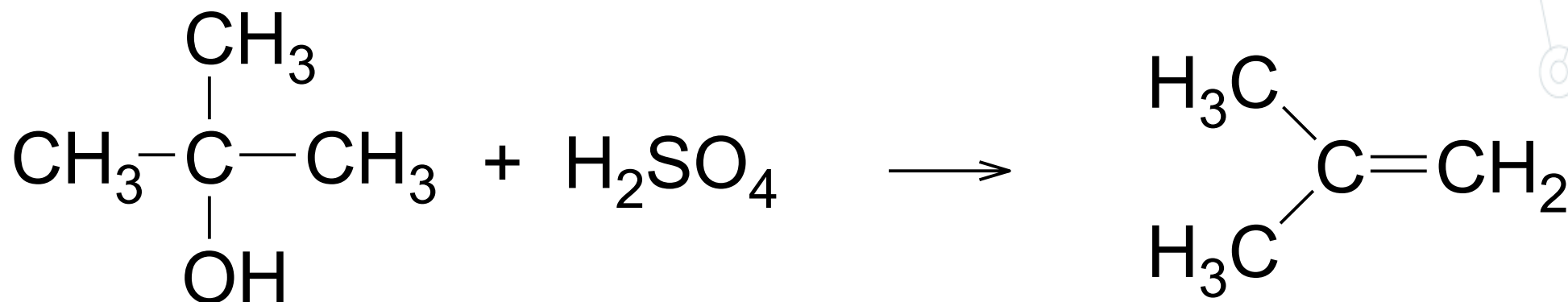
Alkenes are prepared in the laboratory by of the three general methods

- Dehydration of alcohols (presence of acid)
 - Dehydrohalogenation of alkyl halides (presence of base/alcohol)
 - Dehalogenation of vicinal dihalides (presence of Zn/alcohol)
- 

Preparation of Alkenes

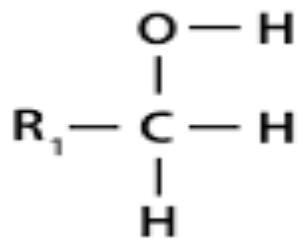
Elimination reaction

1- Dehydration of an Alcohol at higher Temperature/ Al_2O_3

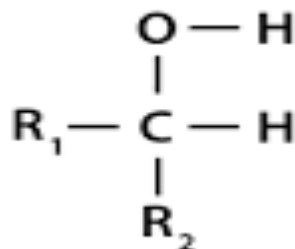


**Primary, Secondary, and
Tertiary Alcohols**

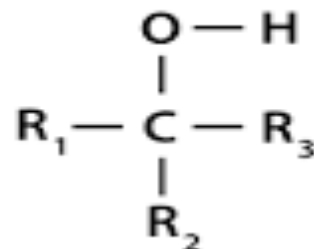
2-methy propene
Or
Isobutene



Primary
Alcohol



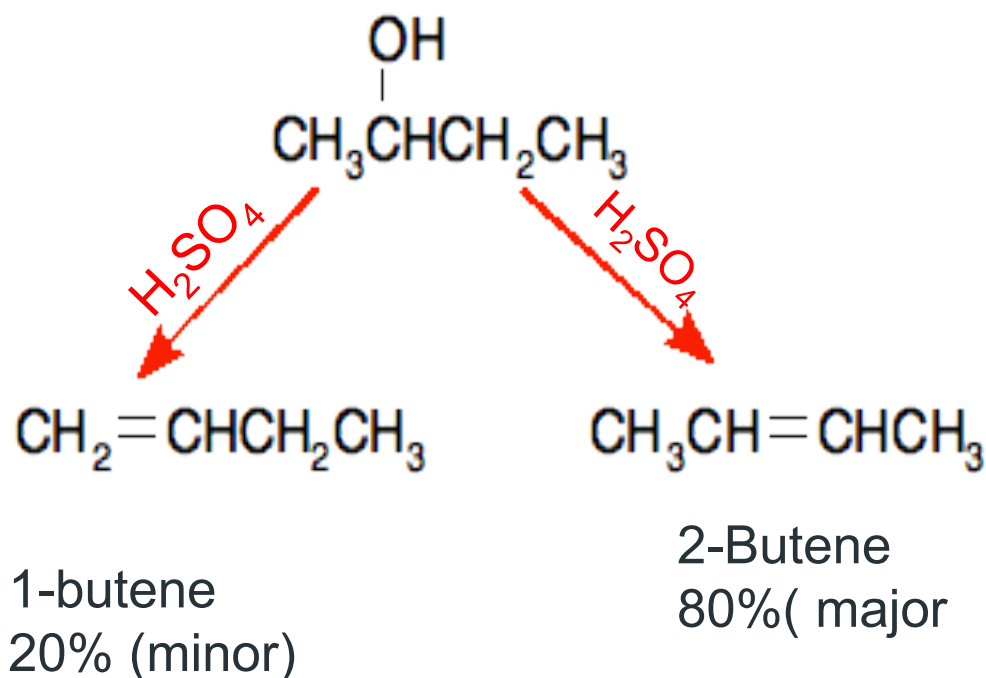
Secondary
Alcohol



Tertiary
Alcohol

Easy of dehydration
 $3^\circ > 2^\circ > 1^\circ$

DEHYDRATION OF UNSYMMETRICAL ALCOHOL

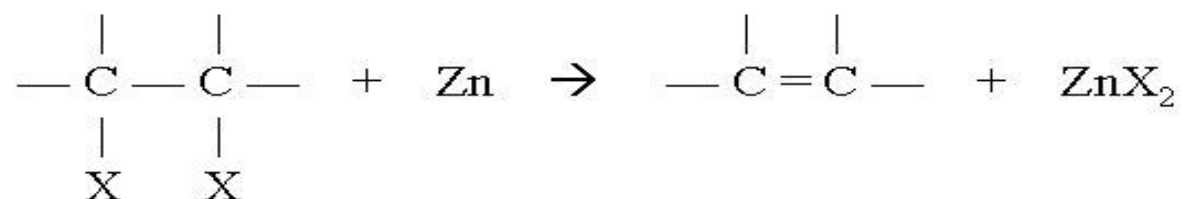


According to saytzeff rule which states that in dehydration the hydrogen is the eliminated from the Carbon with fewer number of H atoms

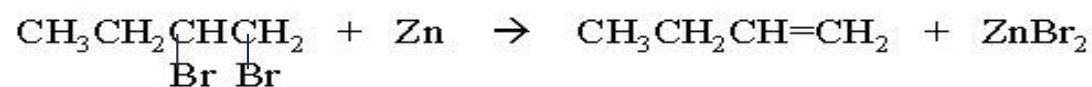
2-DEHALOGENATION OF VICINAL DIHALIDES

Vicinal dihalide

A compound having two halogen atoms on adjacent carbon atoms



eg.



Not generally useful as vicinal dihalides are usually made from alkenes. May be used to “protect” a carbon-carbon double bond.

Reactions of Alkenes

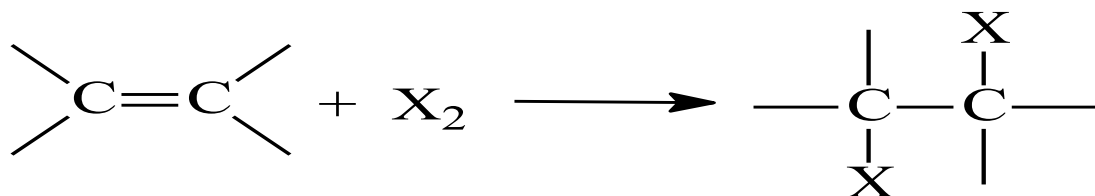
➤ Electrophilic addition reaction

➤ Addition Reactions

- Pi bonds (which are weaker than the C—C bonds), are broken, and new σ bonds are formed to the atoms being added.

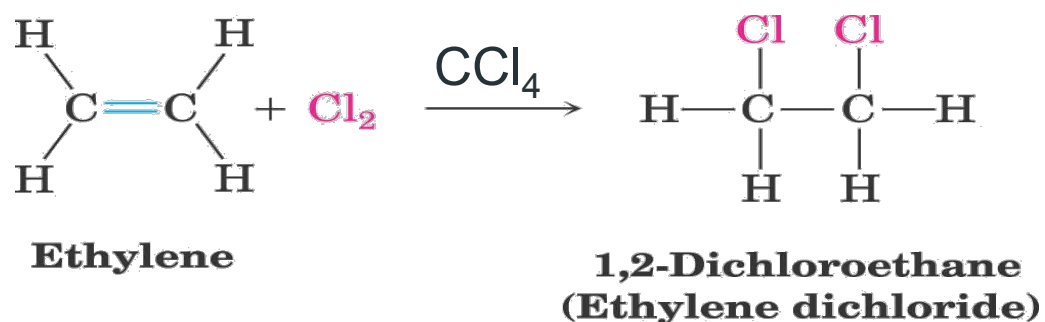
➤ Addition of Halogens (Halogenation)

- Addition of halogen atoms of alkenes and alkynes.

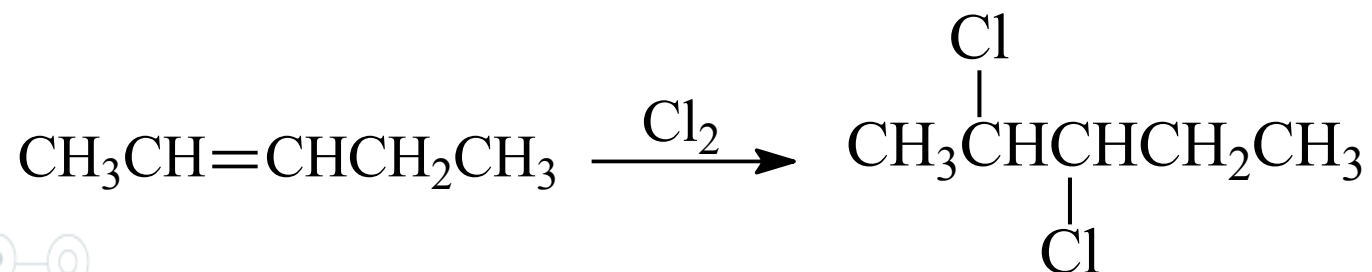
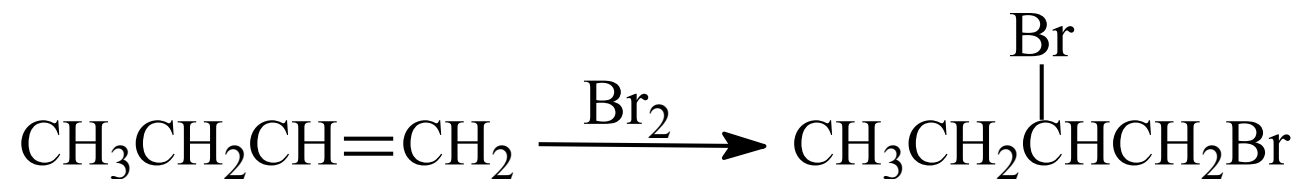


Reactions of Alkenes

❖ Example:



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➤ Addition of hydrogen halide(hydrohalogenation)

Alkene reaction with hydrogen halide according to Markovnikov's rule

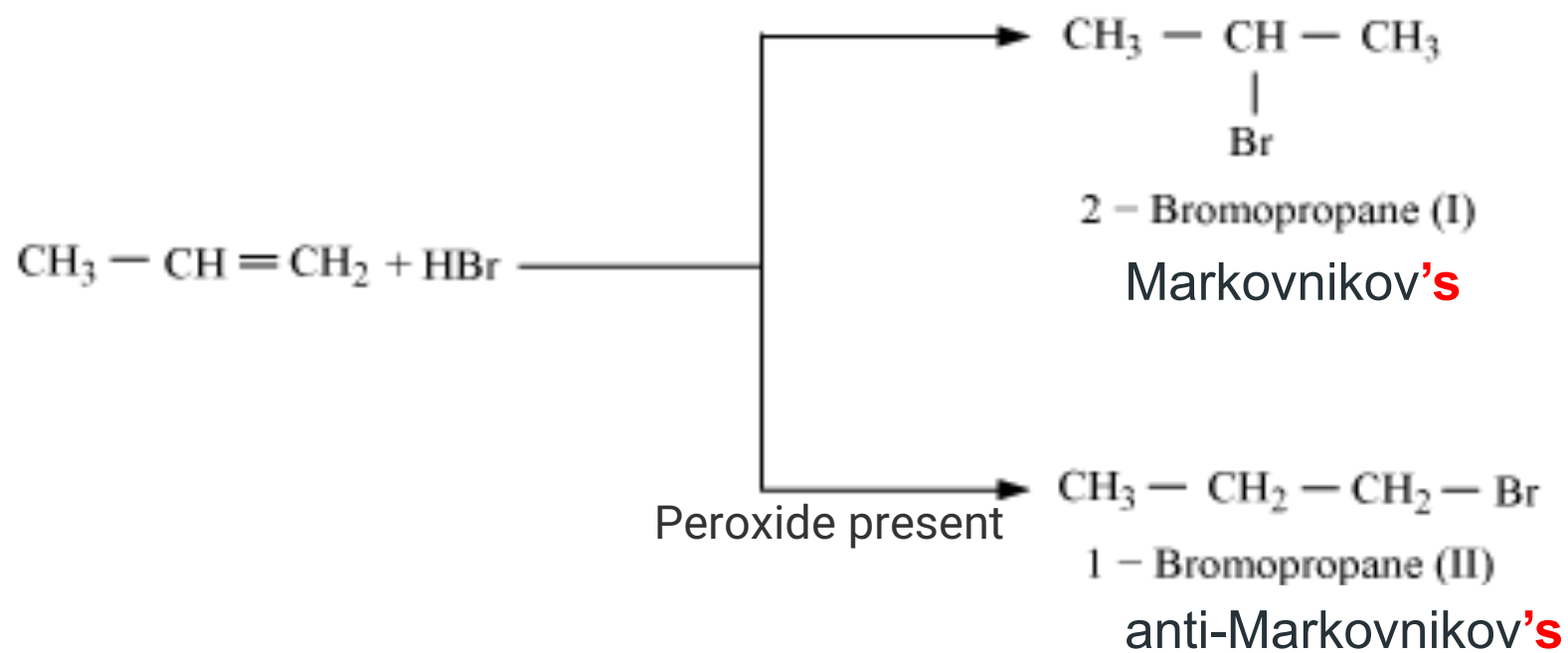
What is Markovnikov's Rule?

- When alkene react with HX the Hydrogen is added to the carbon with the most hydrogens and the halide is added to the carbon with least hydrogens

What is anti-Markovnikov's Rule?

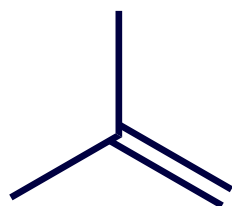
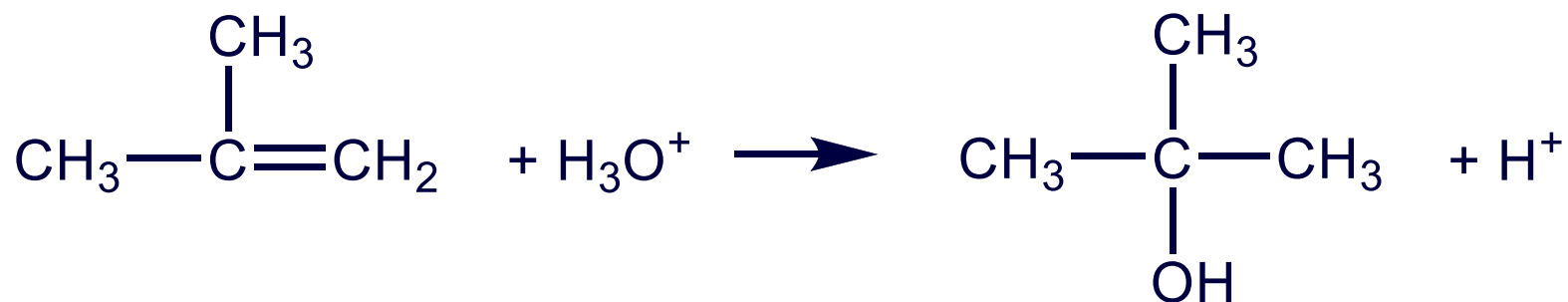
- When alkene react with HX in presence peroxide the Hydrogen is added to the carbon with the least hydrogens and the halide is added to the carbon with most hydrogens

Markovnikov's and anti-Markovnikov's

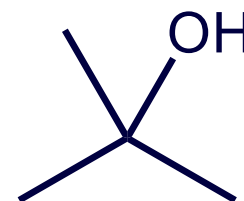


Alkenes

- ❖ Alkenes typically undergo **addition** reactions ($\text{H}_2\text{O}/\text{H}^+$) according to **Markovnikov's Rule**.
- The electron-rich double bond is readily attracted to the partially positive H atoms of H_3O^+ ions and hydrohalic acids.



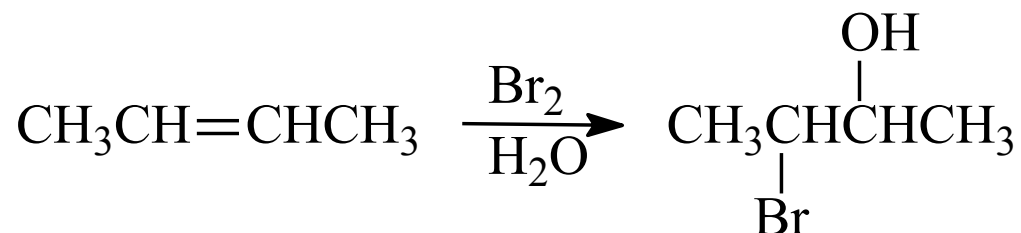
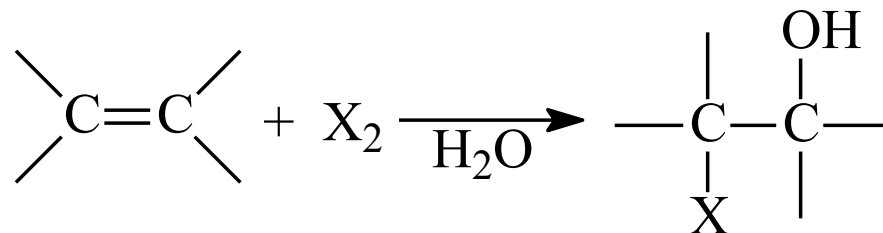
2-methylpropene



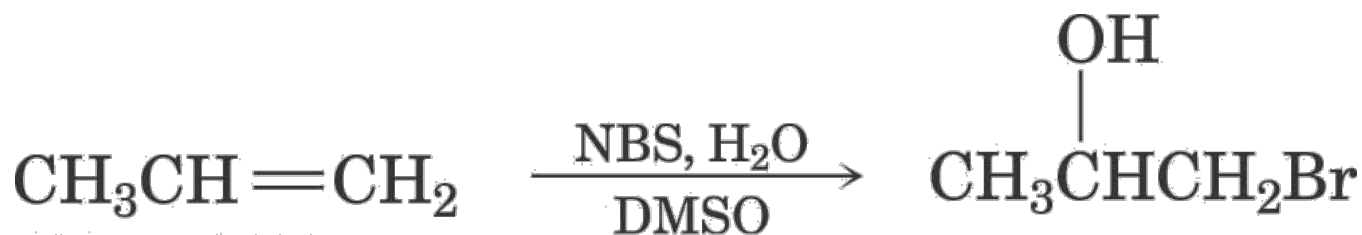
2-methyl-2-propanol

Reactions of Alkenes

➤ Halohydrin Formation



- Orientation of the OH toward the more stable carbocation
(follows **Markovnikov** addition)



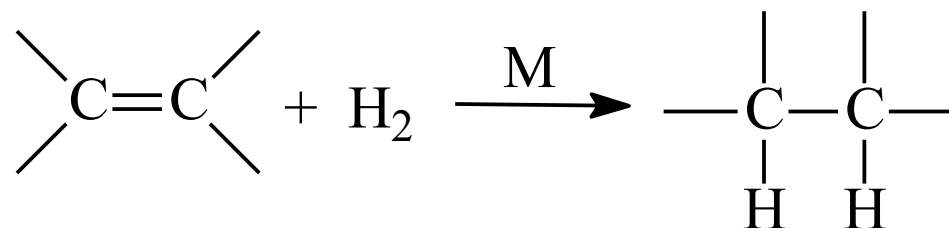
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Reactions of Alkenes

➤ Reduction of Alkenes

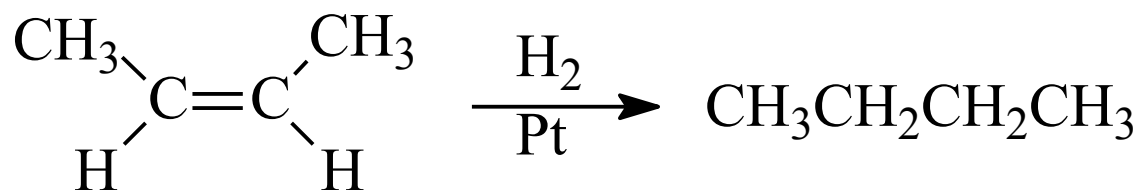
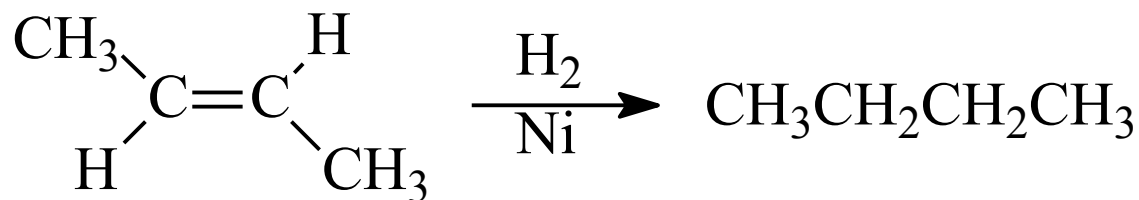
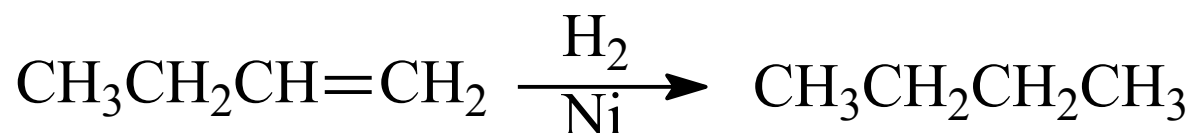
➤ Addition of Hydrogen (Hydrogenation)

- Reduction in general is addition of H_2 or its equivalent Requires Pt, Pd, or Ni as powders on carbon and H_2 Hydrogen is first adsorbed on catalyst Reaction is heterogeneous



M = Pt, Pd, or Ni

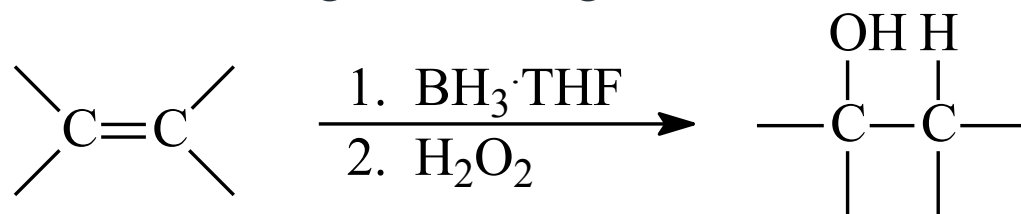
❖ Example:



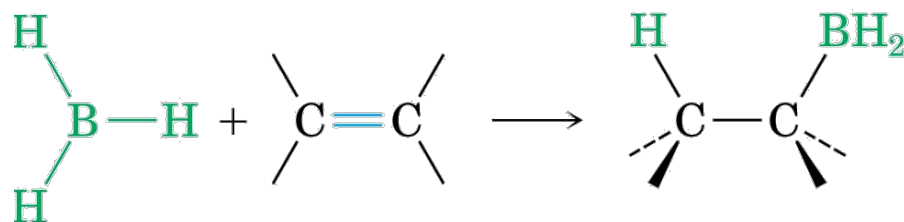
Reactions of Alkenes

➤ Hydroboration-Oxidation

- Herbert Brown invented hydroboration (received the 1979 Nobel Chemistry Prize.)
- Borane (BH_3) is electron deficient is a Lewis acid
- Borane adds to an alkene to give an organoborane



❖ Example:

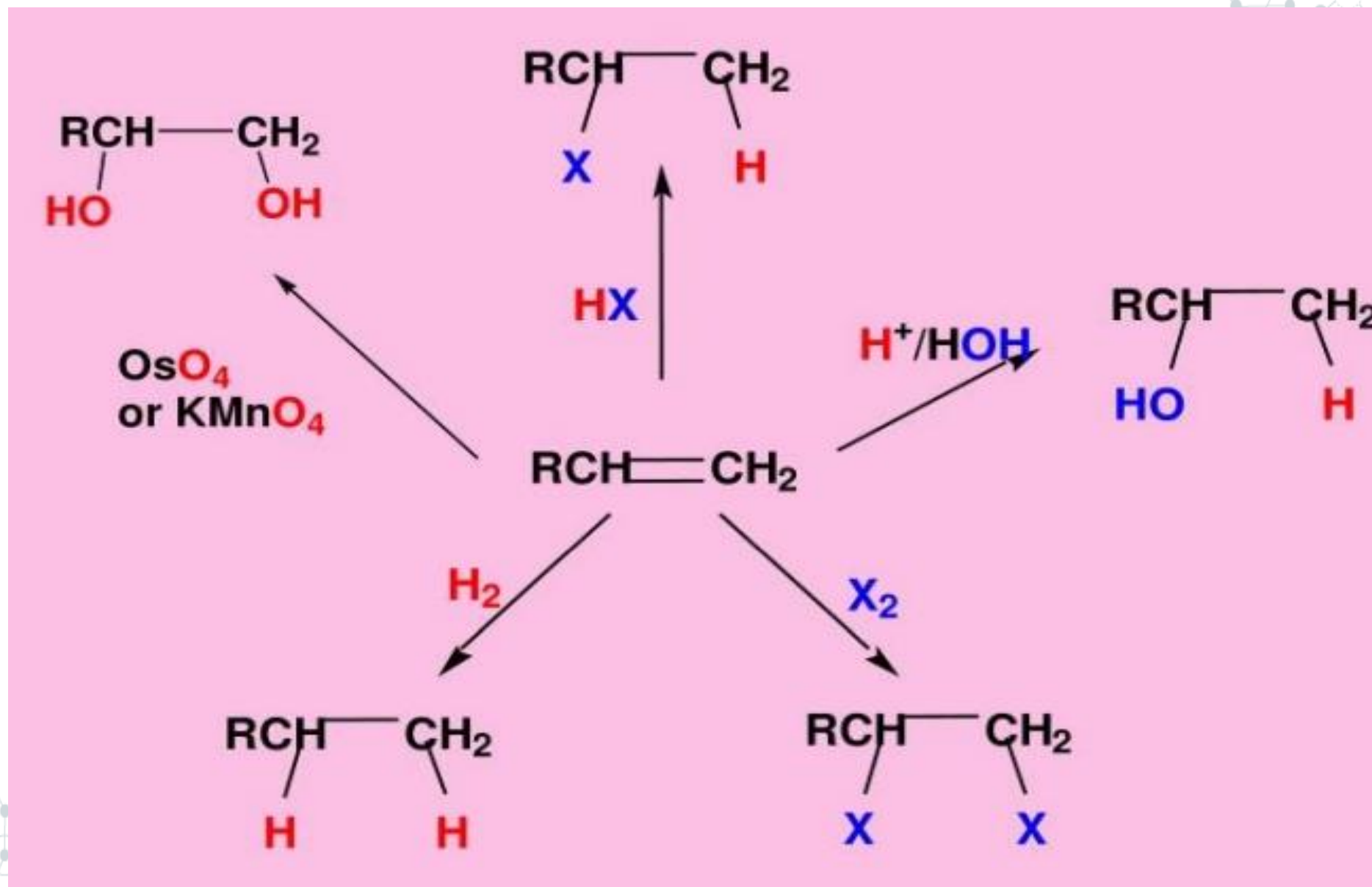


Borane
© Thomson - Brooks Cole

An organoborane

Reactions of Alkenes and Alkynes

➤ Addition Reactions Summary



Hydrocarbons

➤ 3. alkyne

- An **alkyne** is a hydrocarbon that contains at least one **$\text{C}\equiv\text{C}$** triple bond.
- Alkynes have the general formula **$\text{C}_n\text{H}_{2n-2}$** and they are also considered **unsaturated** carbons.
- Alkynes are named in the same way as alkenes, using the **suffix $-\text{yne}$** .

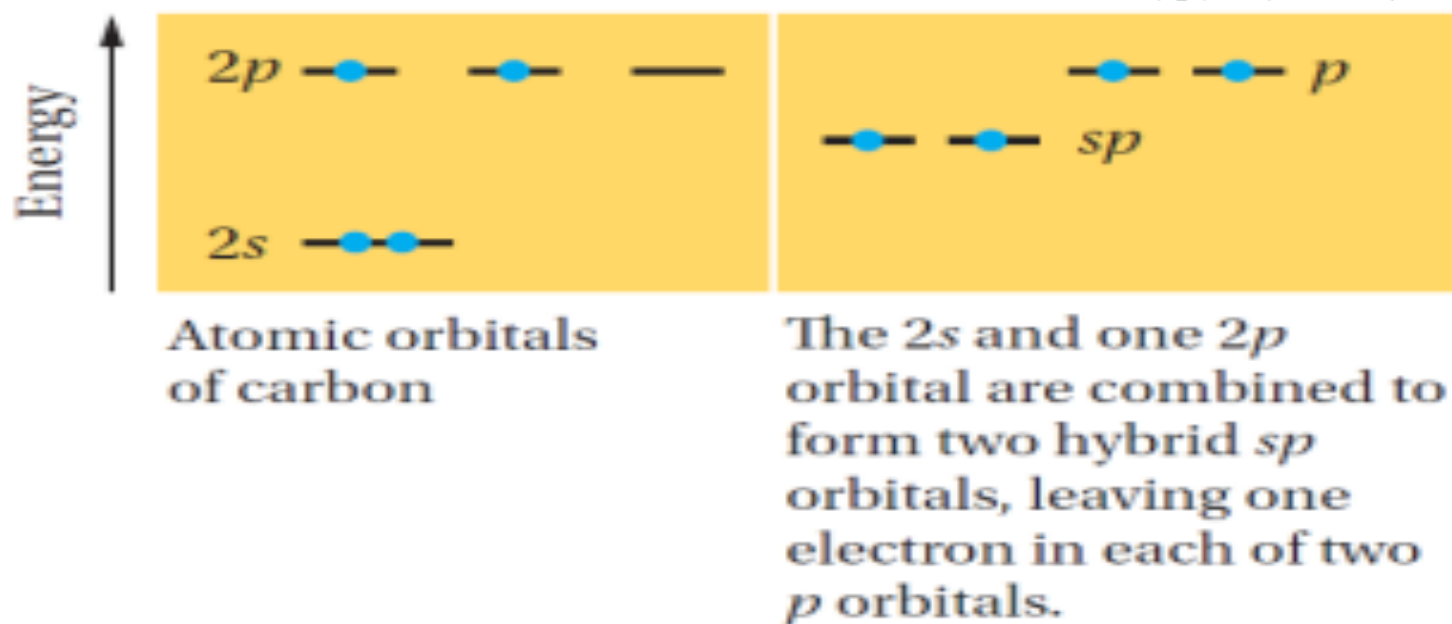
The Strengths of Bonds

- Double and triple bonds contain more than one bond.
- First bond is always strongest.
- Second and third bonds are weaker: therefore, react faster
 - C=C bonds are than C-C bonds.

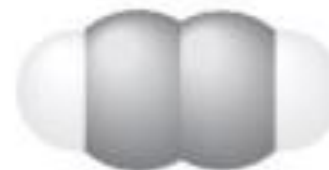
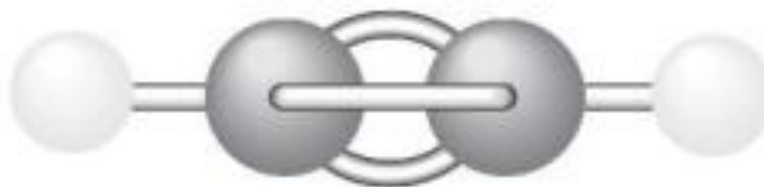
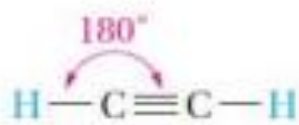
Hydrocarbons

➤ Hybridization (Alkynes sp):

- The carbon atom of an acetylene is connected to only two other atoms. Therefore, we combine the $2s$ orbital with only one $2p$ orbital to make two sp -hybrid orbitals



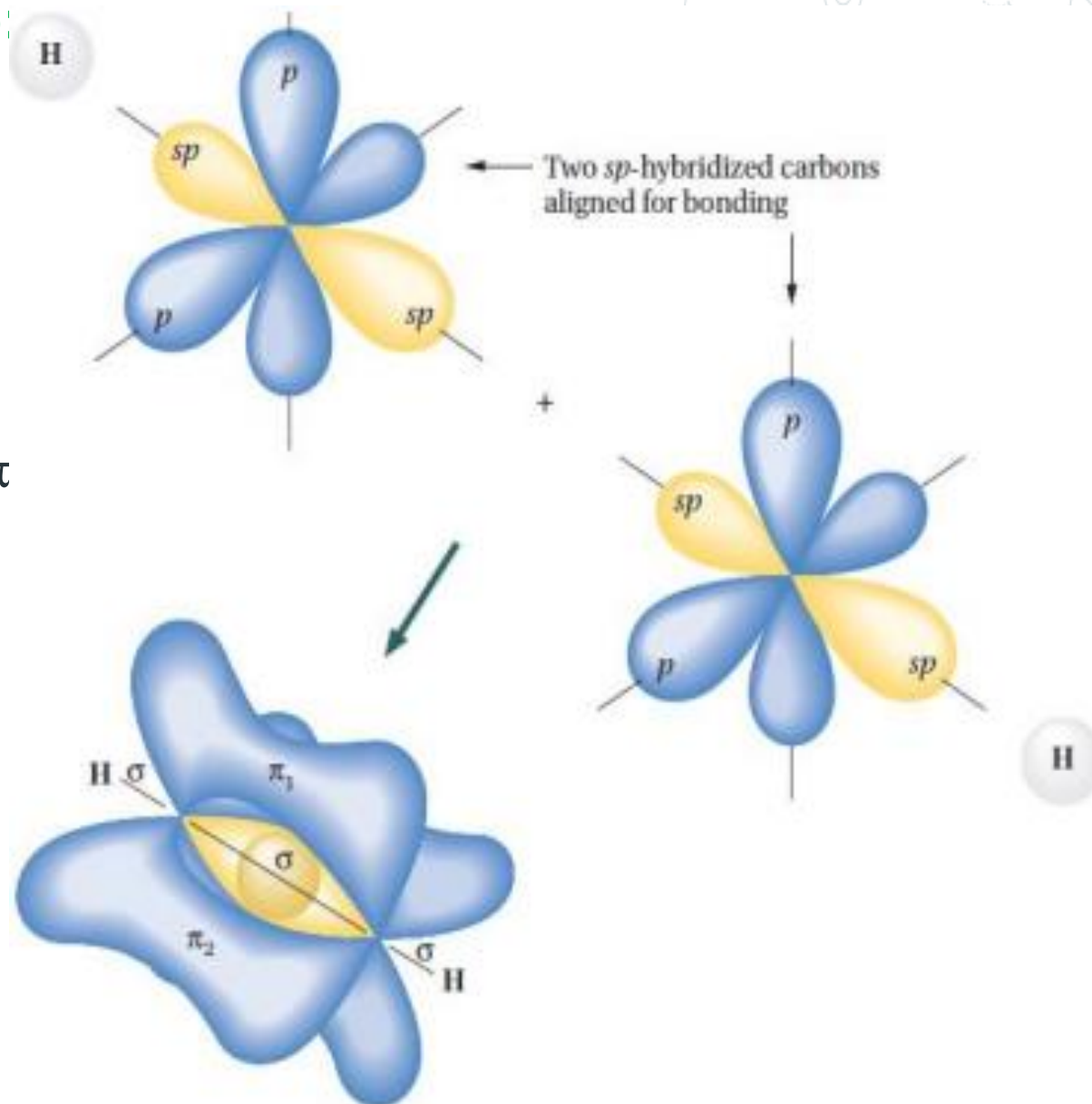
- The angle between the two hybrid orbitals is 180°
- Linear



Hydrocarbons

➤ Hybridization (Alkynes sp)

- A triple bond consists of the end-on overlap of two sp -hybrid orbitals to form a σ bond and the lateral overlap of two sets of parallel oriented p orbitals to form two mutually perpendicular π bonds

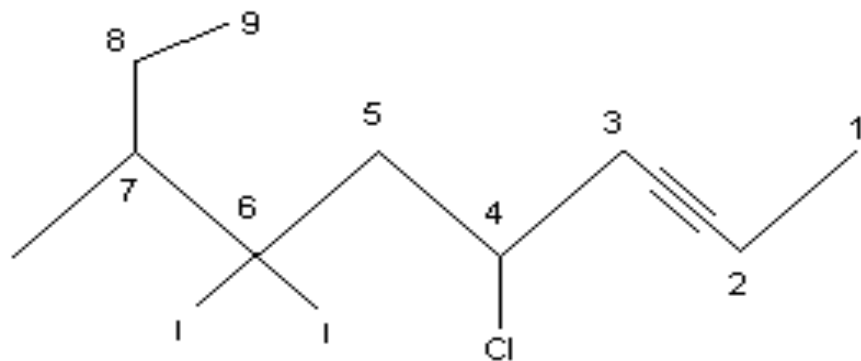


NAMENCULTURE OF ALKYNE

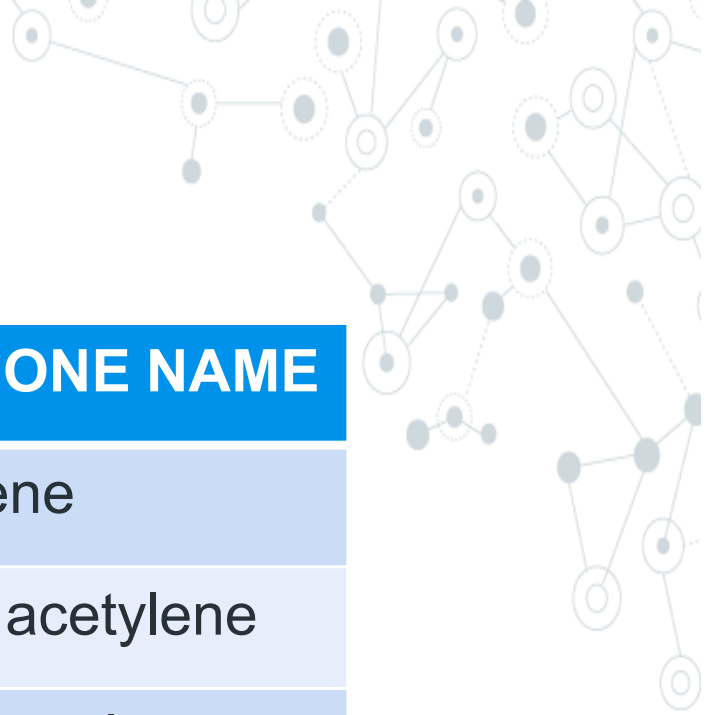
- Like alkenes have the suffix –ene, alkynes use the ending –yne

RULE :

- 1- Find the longest carbon chain that includes both carbons of the triple bond
- 2- Number the longest chain starting at the end closest to the triple bond.
- 3- After numbering the longest chain with the lowest number assigned to the alkyne, label each of the substituents at its corresponding carbon



4-chloro-6-diiodo-7-methyl-2-nonyne



FORMULA	IUPAC	COMMON NAME
$\text{CH} \equiv \text{CH}$	Ethyne	Acetylene
$\text{CH}_3\text{C} \equiv \text{CH}$	Propyne	Methyl acetylene
$\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$	1-Butyne	Ethyl acetylene
$\text{CH}_3\text{C} \equiv \text{CCH}_3$	2-Butyne	Dimethyl acetylene
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH}$	1-Pentyne	Propyl acetylene



PHYSICAL PROPERTIES OF ALKYNE

- Alkyne from C₂-C₃ are gases, C₃-C₈ are liquid and above the C₉ is solid
- Alkynes are slightly soluble in water because of low polarity but soluble in organic solvent
- Lower members are poisonous in nature
- The melting point and boiling point rise with increase in molecular weight
- Branch chain alkynes have lower boiling point than straight chain
- Alkynes have higher melting point than alkanes and alkenes

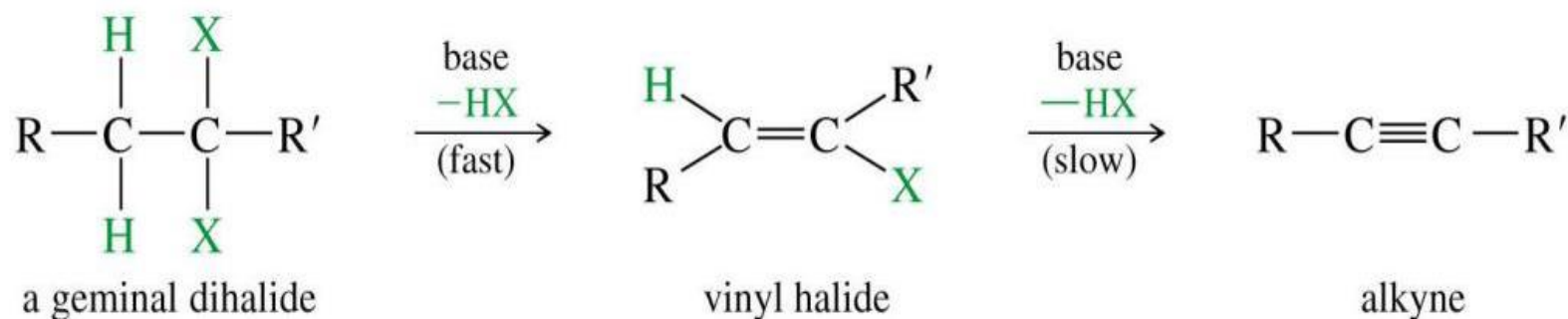
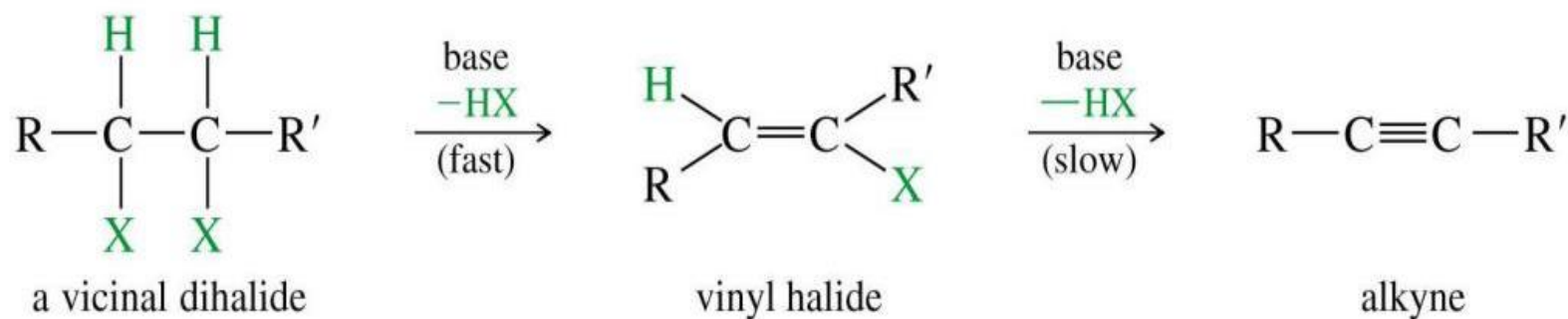
PREPARATION OF ALKYNE

Synthesis of alkyne by double dehydrohalogenation

- Loss of two molecules of HX from a vicinal or geminal dihalide

Geminal

A compound having two halogen atoms are attached to the same carbon atoms

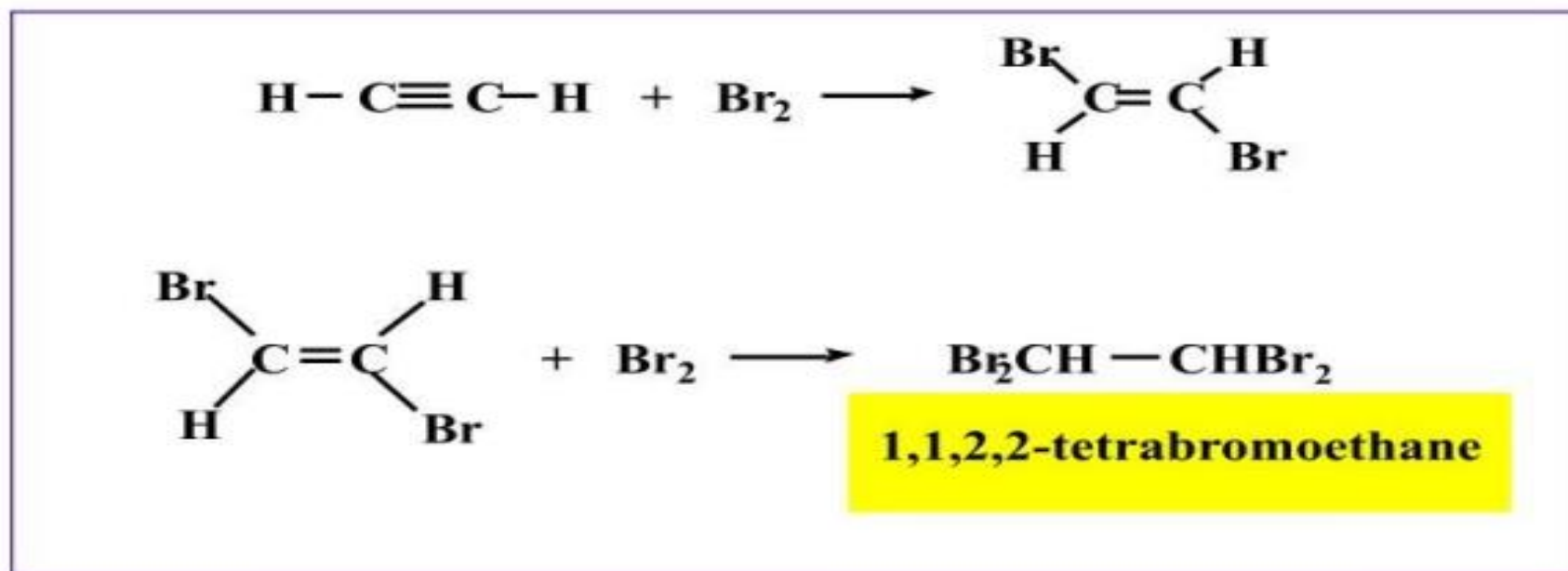


Reactions of Alkynes

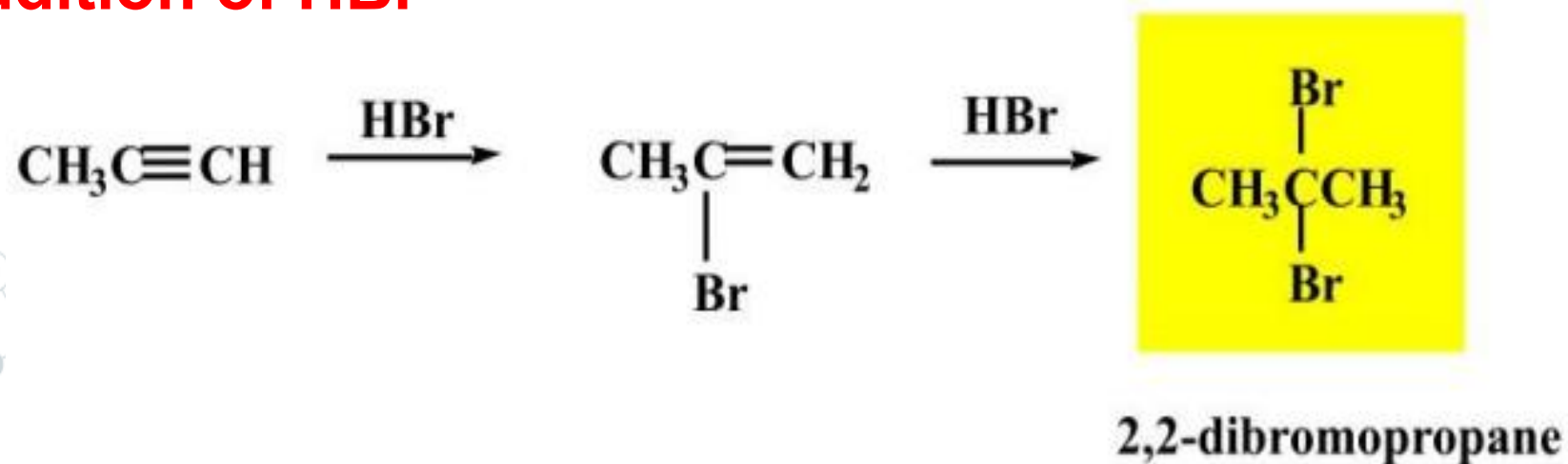
- Very similar to alkenes:
 - They add halogens twice, X_2
 - They add hydrogen halides twice, HX
 - They add hydrogen twice, H_2
 - They add water with acid (hydration)
 - Markovnikov's rule applies
- They are slightly acidic and react with strong bases

Reactions of Alkynes

➤ Addition of Bromine

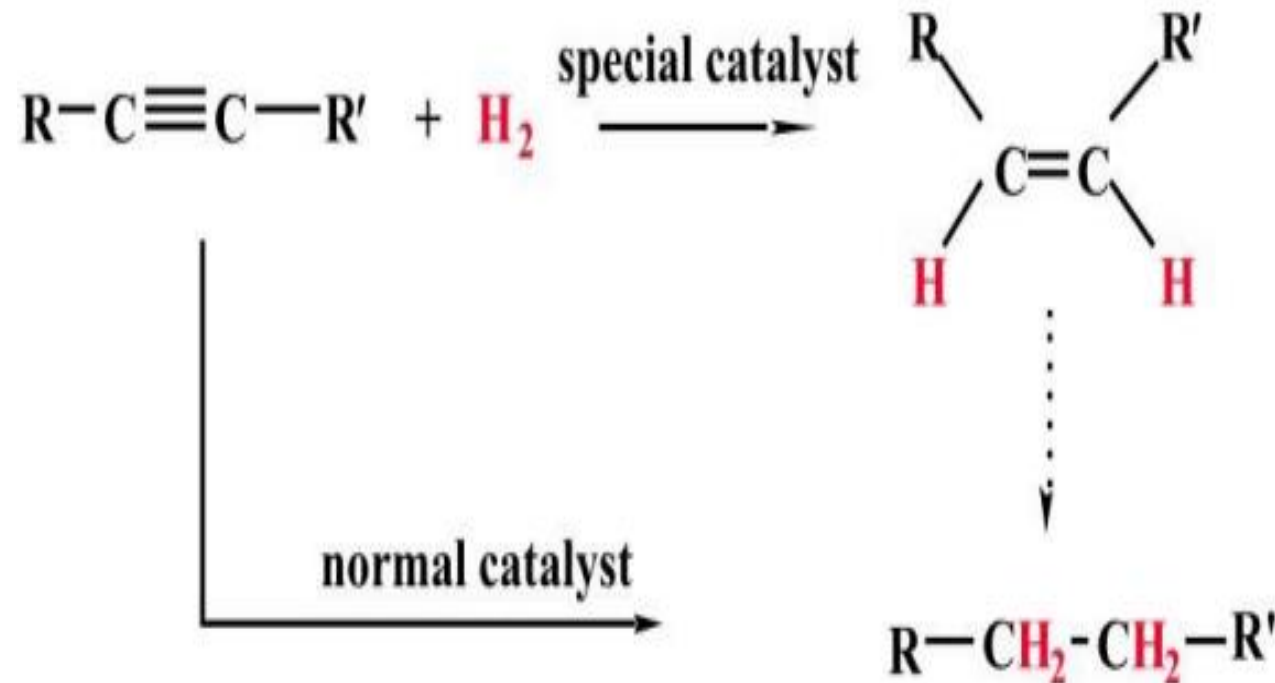


➤ Addition of HBr

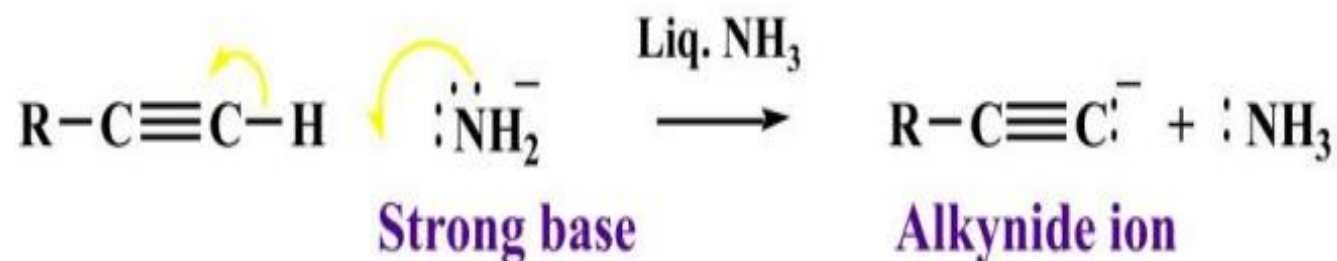


Reactions of Alkynes

➤ Addition of H_2



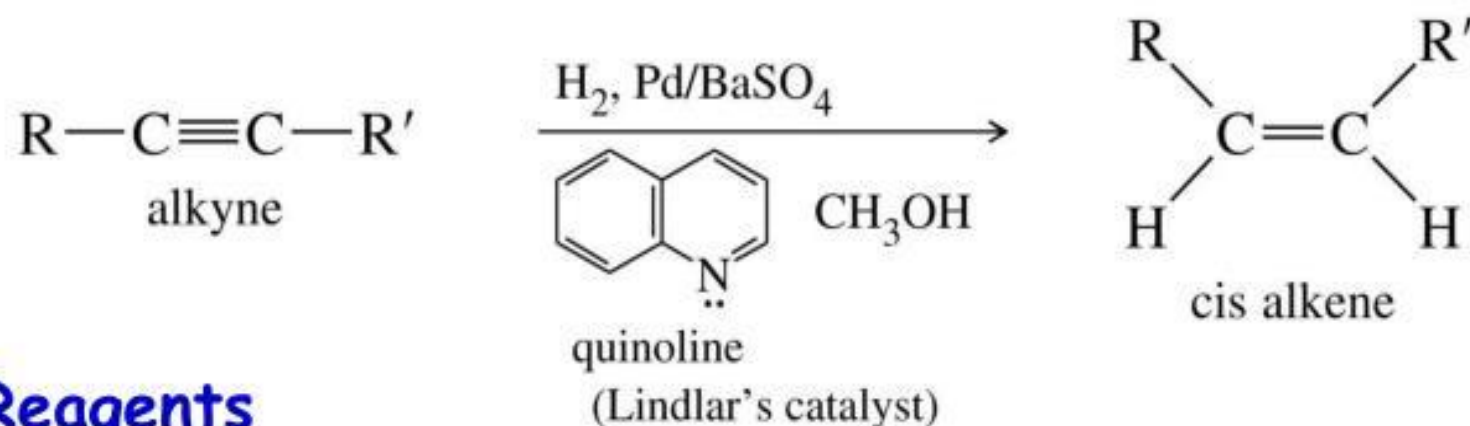
➤ Reactions as an acid



- Very strong base required

Reactions of Alkynes

- **Catalytic Hydrogenation to cis-Alkene**
 - formation of cis-alkene using a poisoned (partially deactivated) catalyst

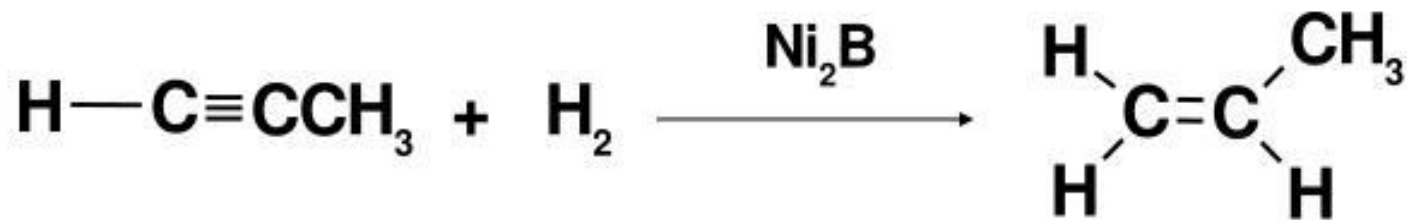


■ Reagents

- OR {
- H_2
 - Lindlar's catalyst ($\text{Pd/BaSO}_4/\text{quinoline}$)
 - Ni_2B (nickel boride)

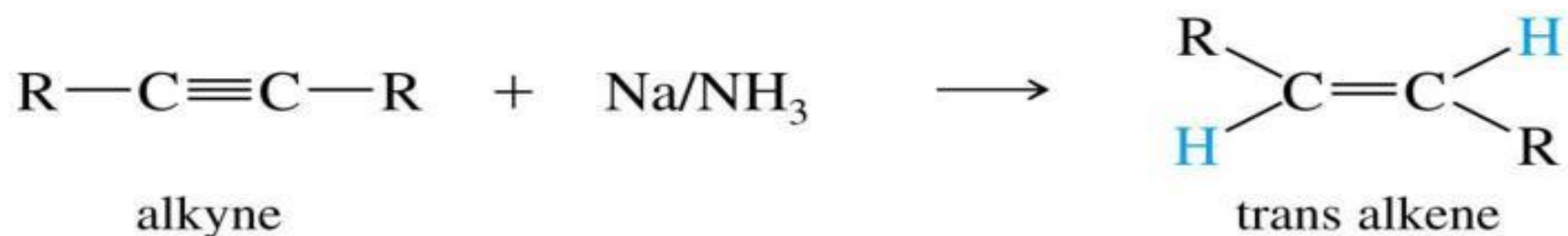
Reactions of Alkynes

■ Examples:

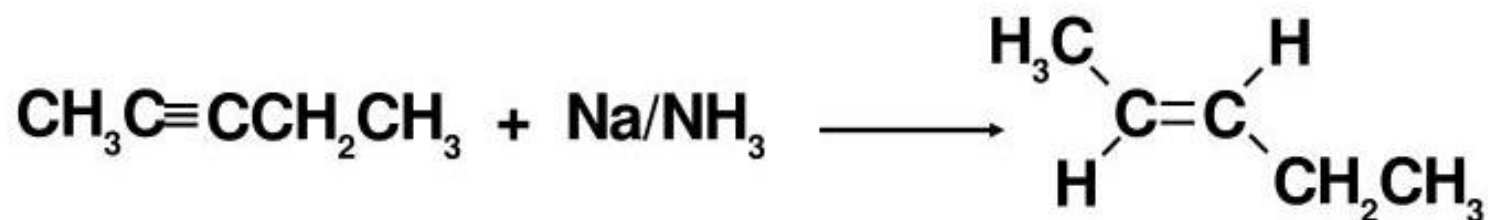


Reactions of Alkynes

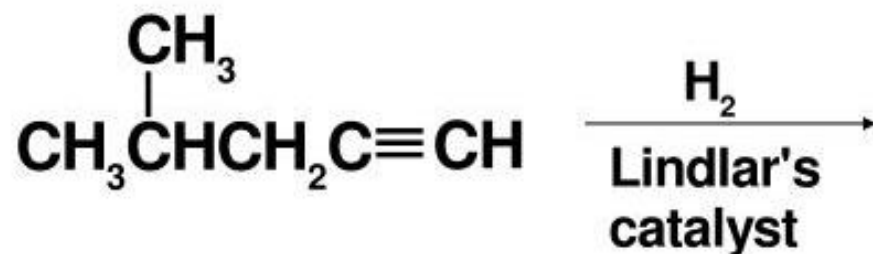
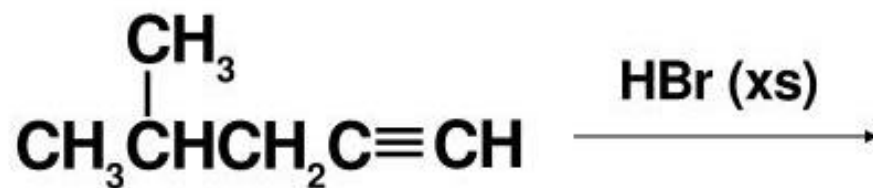
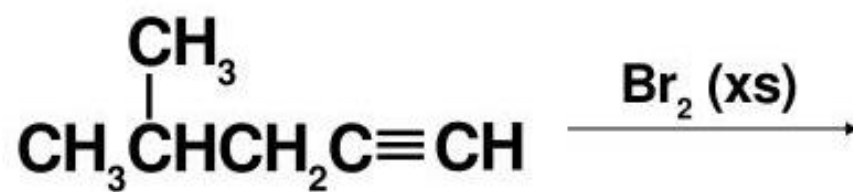
- **Metal-NH₃ Reduction to trans-Alkene**
 - formation of trans-alkene using Na/NH₃
 - involves radical anion and radical intermediates



- trans isomer forms because the trans radical intermediate is more stable



Predict the product of the following reactions?



Hydrocarbon derivatives

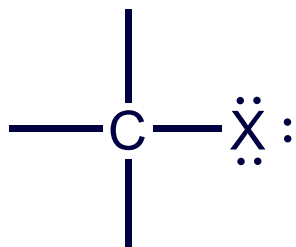


- Molecules that are fundamentally hydrocarbons but have additional atoms or groups of atoms called functional groups.

- ALKYL HALIDE
 - ALCOHOL
 - ETHER
 - ALDEHYDE AND KETONE
 - CARBOXYLIC ACID
 - ESTER
 - AMINE
- 

Haloalkanes

- Haloalkanes or *alkyl halides* contain a *halogen* atom bonded to carbon.

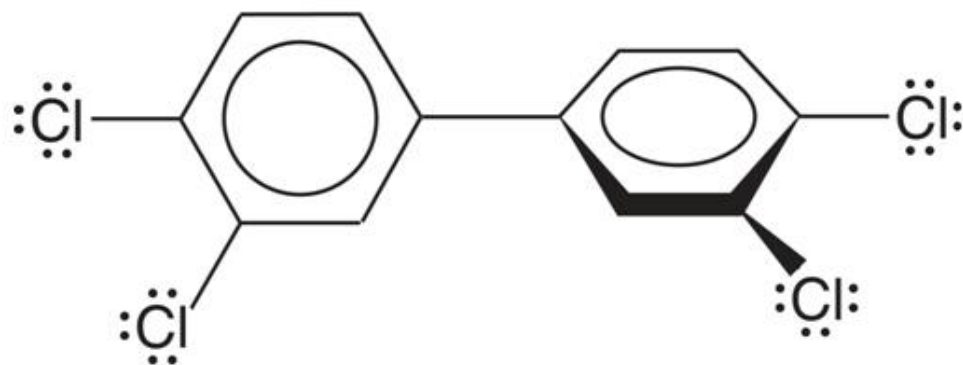
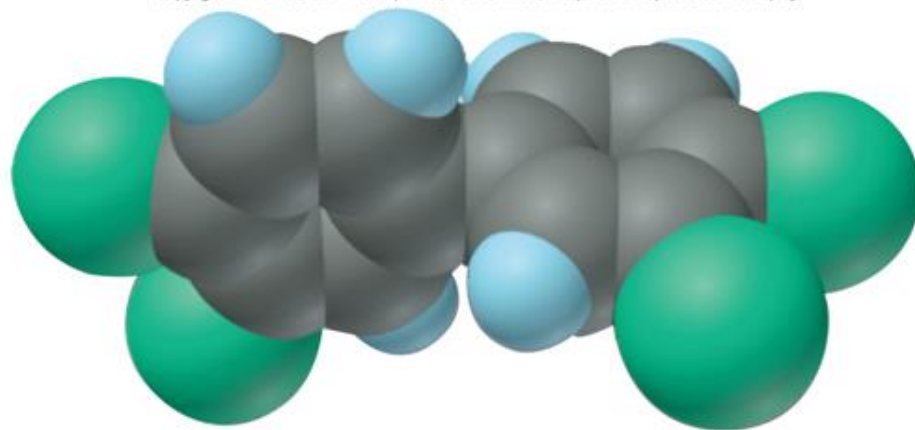


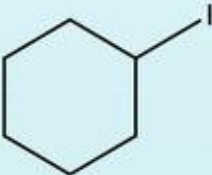
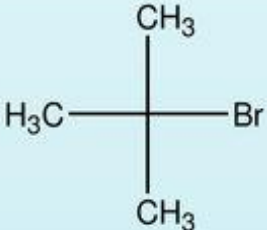
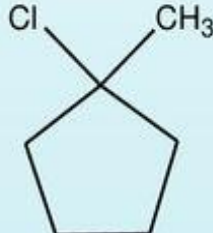
- The general formula is $\text{C}_n\text{H}_{2n+1}\text{X}$ or RX
- Haloalkanes are named by identifying the **halogen** with a **prefix** on the hydrocarbon name. The C bearing the halogen must be **numbered**.
- CH_3Cl the name is chloromethane

Haloalkanes

- ❖ A tetrachlorobiphenyl, one of 209 polychlorinated biphenyls (PCBs).

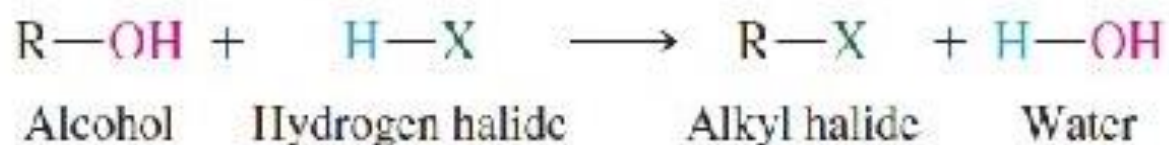
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<u>1-Alkyl halides</u> (R-X):	$\text{CH}_3\text{-Cl}$	$\text{CH}_3\text{-CH}_2\text{-Br}$	$(\text{CH}_3)_2\text{-CH-F}$
Common	Methyl Chloride	Ethyl bromide	Isopropyl fluoride
IUPAC	Chloromethane	Bromoethane	2-Fluoropropane
Class	1°	1°	2°
			
Common	Cyclohexyl Iodide	t. Butyl bromide	Methylcyclopentyl chloride
IUPAC	Iodocyclohexane	2-Bromo-2-methylpropane	1-Chloro-1-methylcyclopentane
Class	2°	3°	3°

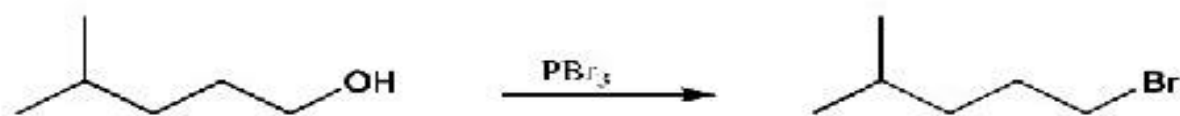
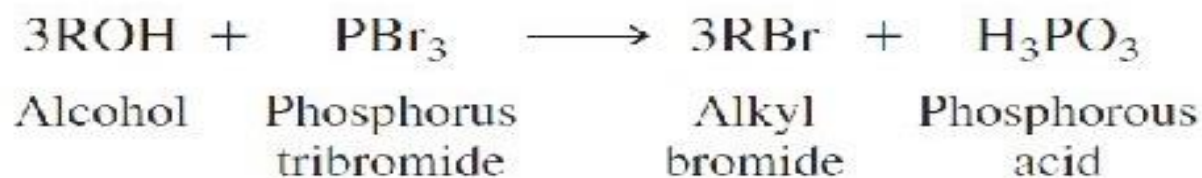
PREPARATION OF ALKYL HALIDE

Reaction of alcohols with hydrogen halides yields alkyl halides:



Reaction of Alcohols with Phosphorous Tribromide

Phosphorous tribromide (PBr_3) reacts with alcohols to form alkyl bromides. This is also an $\text{S}_{\text{N}}2$ reaction.



PHYSICAL PROPERTIES

- Chloromethane and bromomethane and chloroethane are gases Iodomethane is liquid
- All organic halides are insoluble in water and soluble in common organic solvents.
- In an alkyl halide, the halogen is more electronegative than carbon
- The boiling points increases with increasing in molecular weights.
- Alkyl halides have higher melting point than the corresponding alkanes, alkenes, and alkynes because:

1. Polarity

2. Molecular weight **(In series of halides BP. $F < Cl < Br < I$)**



bp= 47°C



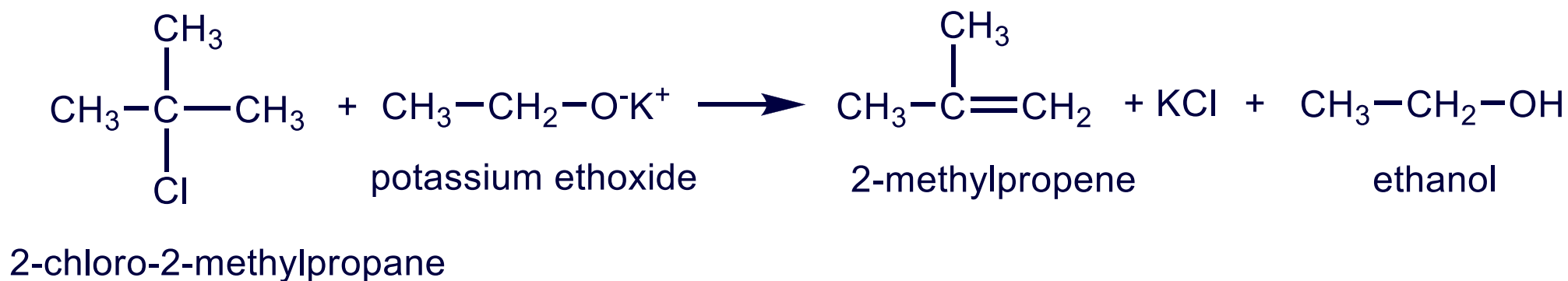
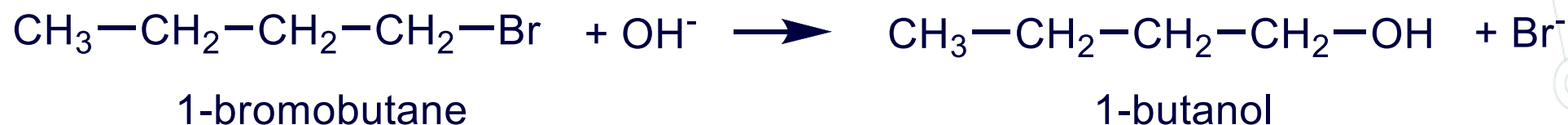
bp= 71°C



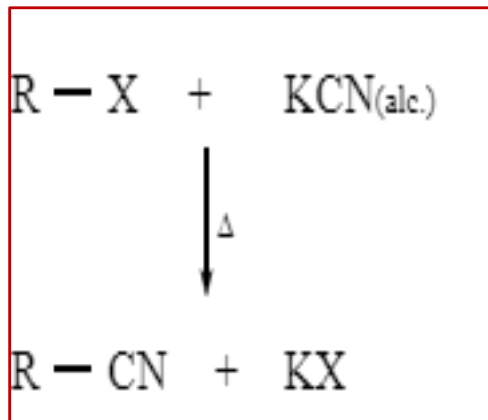
bp= 102°C

Reactions of Haloalkanes

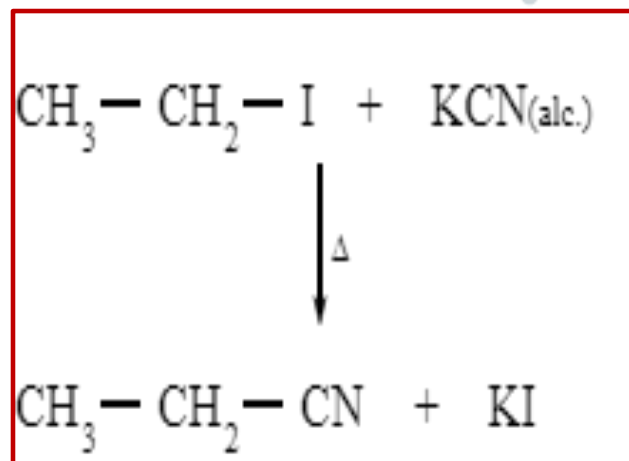
❖ Haloalkanes undergo **substitution** and **elimination** reactions.



- **With potassium cyanide (KCN) to form Alkyl cyanide (nitrile)**

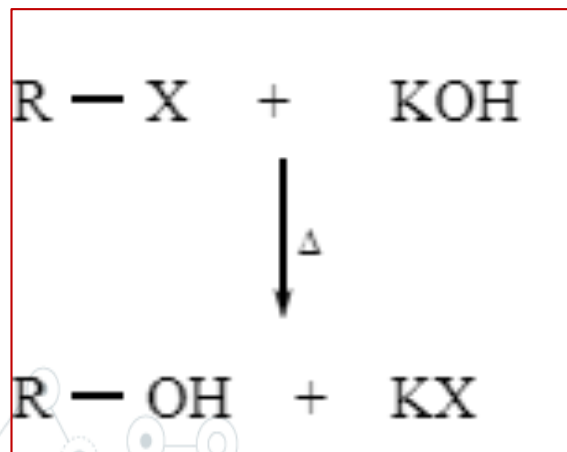


EXAMPLE :

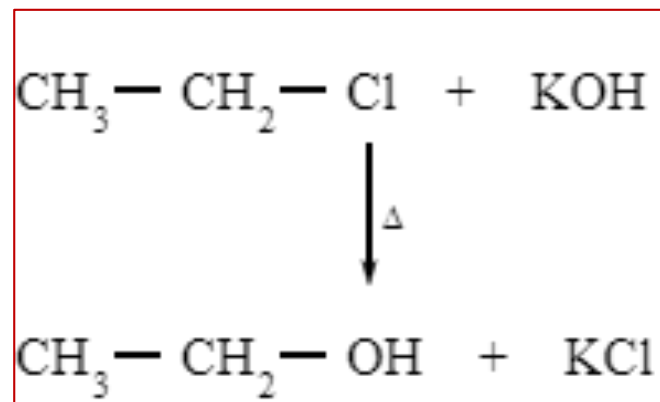


- **Reaction of Haloalkanes with Aqueous Alkali**

Haloalkanes react with boiling aqueous alkalies to produce alcohols. The general reaction and an example are given below

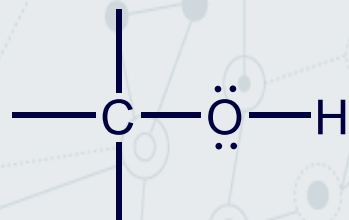


EXAMPLE

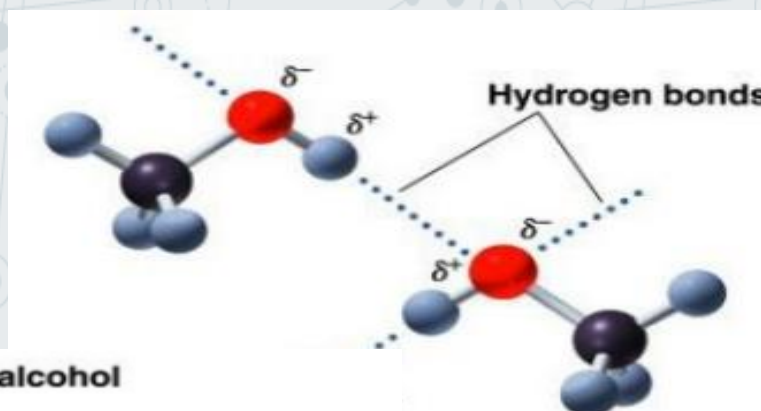


□ Alcohols

- The *alcohol* functional group consists of a carbon bonded to an **-OH** group.

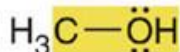


- Alcohols are named by replacing the *-e* at the end of the parent hydrocarbon name with the **suffix -ol**.
- Alcohols have **high** melting and boiling points since they can form hydrogen bonds between their molecules.



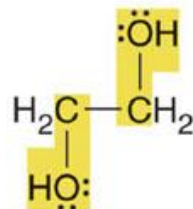
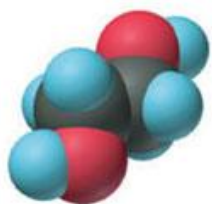
Alcohols

□ Some molecules with the alcohol functional group.



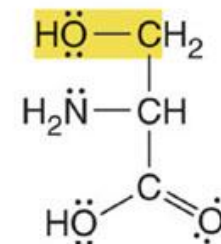
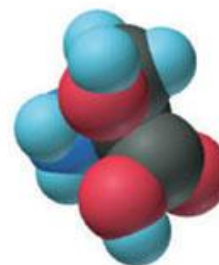
Methanol (methyl alcohol)

By-product in coal gasification; de-icing agent; gasoline substitute; precursor of organic compounds



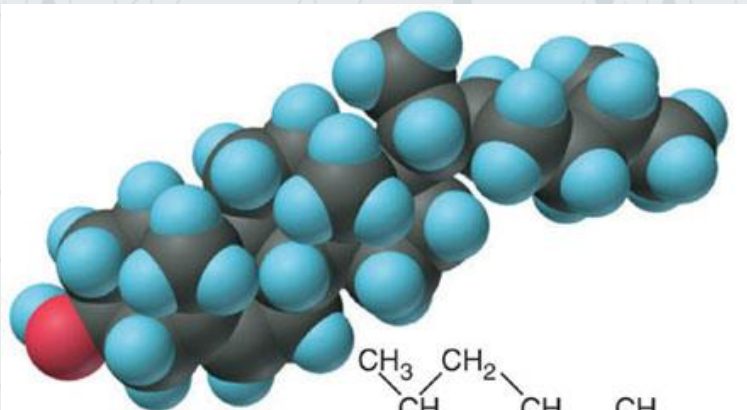
1,2-Ethanediol (ethylene glycol)

Main component of auto antifreeze



Serine

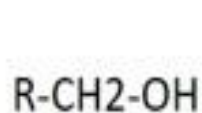
Amino acid found in most proteins



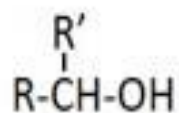
Cholesterol

Major sterol in animals; essential for cell membranes; precursor of steroid hormones

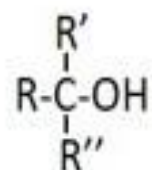
Naming alcohols:



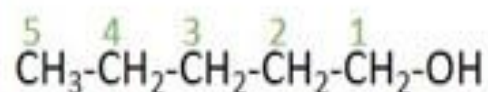
Primary alcohol



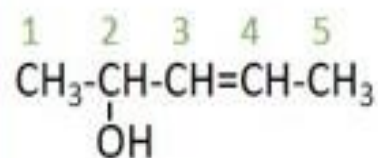
Secondary alcohol



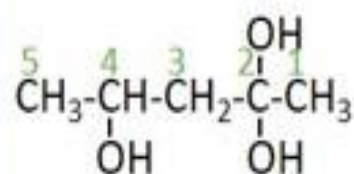
Tertiary alcohol



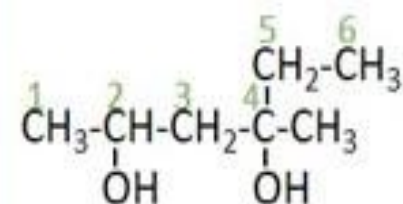
1-Pentanol



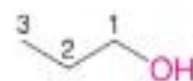
3-Penten-2-ol



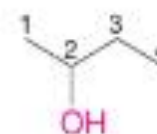
2,2,4-Pentanetriol



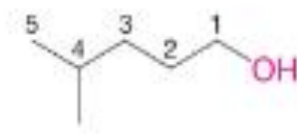
4-Methyl-2,4-hexanediol



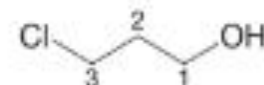
1-Propanol



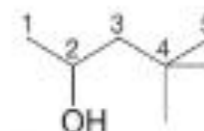
2-Butanol



4-Methyl-1-pentanol
or 4-methylpentan-1-ol
(not 2-methyl-5-pentanol)



3-Chloro-1-propanol
or 3-chloropropan-1-ol



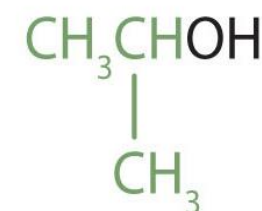
4,4-Dimethyl-2-pentanol
or 4,4-dimethylpentan-2-ol



Propyl alcohol



Methyl alcohol

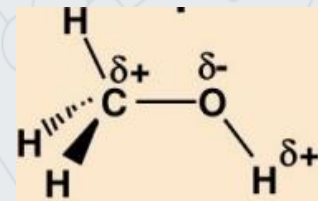


Isopropyl alcohol



Ethyl alcohol

Alcohols



- ❑ Alcohols are polar compounds.
- ❑ Alcohols are associated in the liquid state by hydrogen bonding

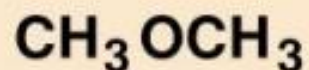
- **Hydrogen bonding:** the attractive force between a partial positive charge on hydrogen and a partial negative charge on a nearby oxygen, nitrogen, or fluorine atom

- Their boiling points are dramatically different
 - ethanol forms intermolecular hydrogen bonds which increases attractive forces between its molecules, which results in a higher boiling point



Ethanol

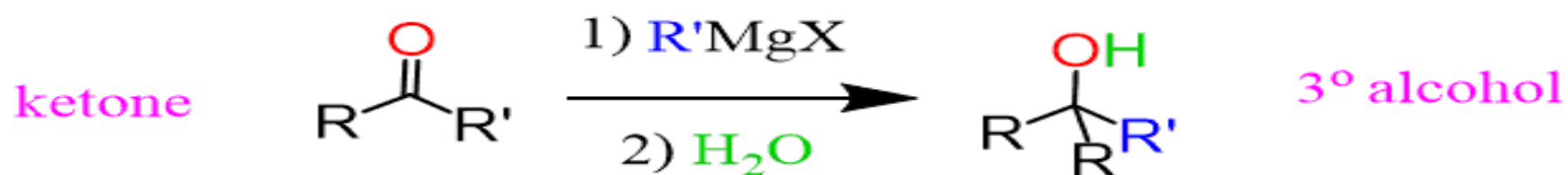
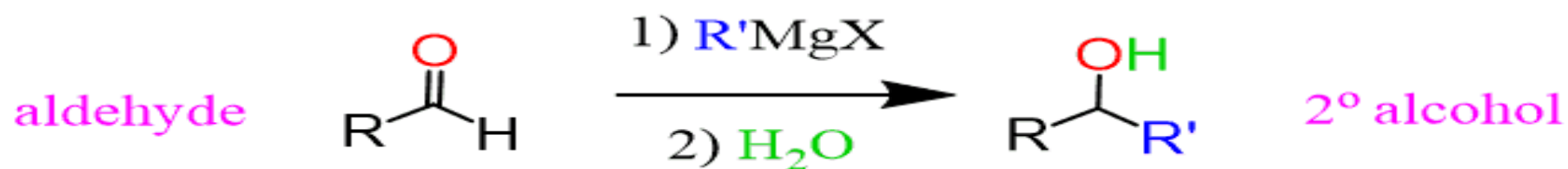
bp 78°C



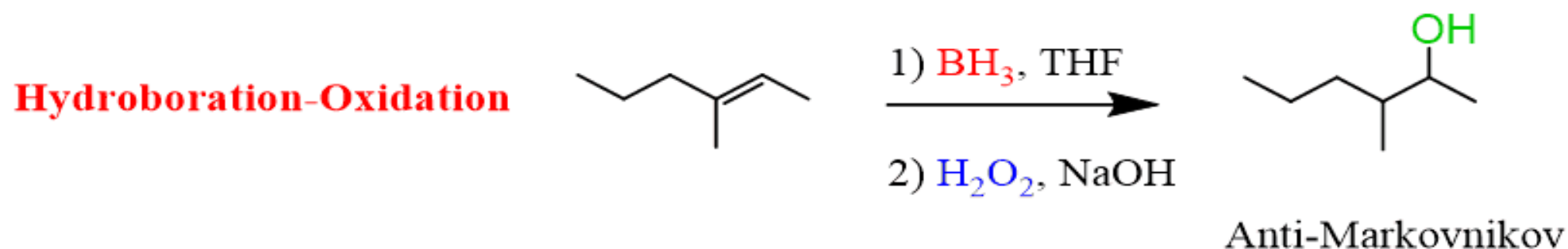
Dimethyl ether

bp -24°C

Preparation of Alcohols by Grignard Reactions

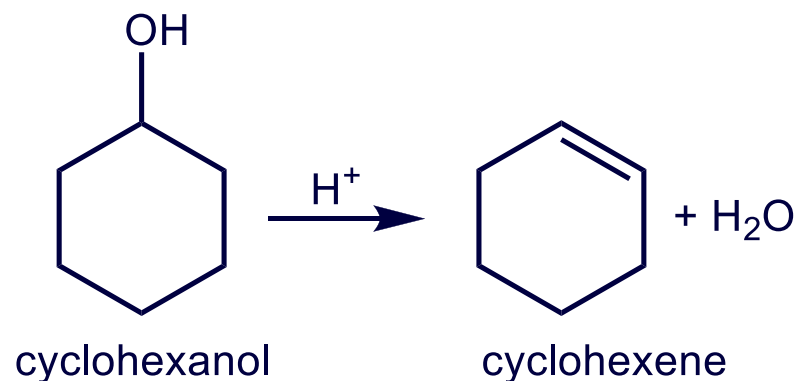


Preparation of Alcohols by Addition Reaction to Alkenes



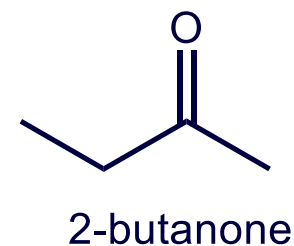
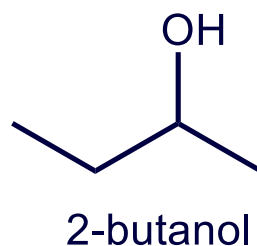
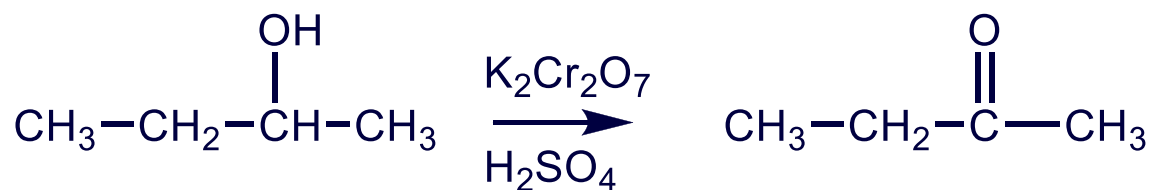
Reactions of Alcohols

❖ Alcohols undergo **elimination** and **substitution** reactions.



dehydration (**elimination**)

oxidation
(**elimination**)

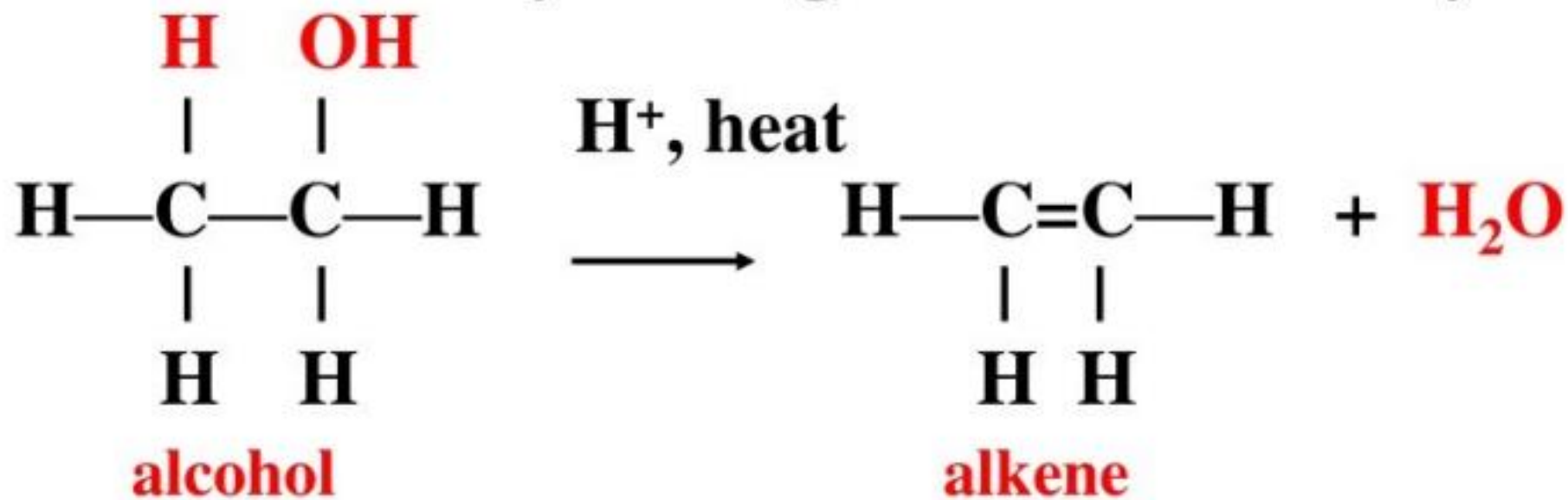


Reactions of Alcohols

- Alcohols undergo **combustion** with O_2 to produce CO_2 and H_2O .



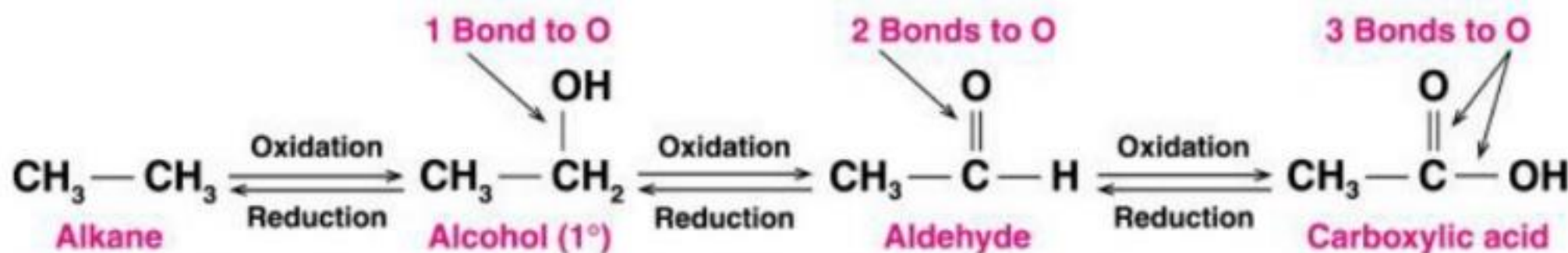
- Dehydration** removes H- and -OH from *adjacent* carbon atoms by heating with an acid catalyst.



Reactions of Alcohols

❖ Oxidation and Redaction

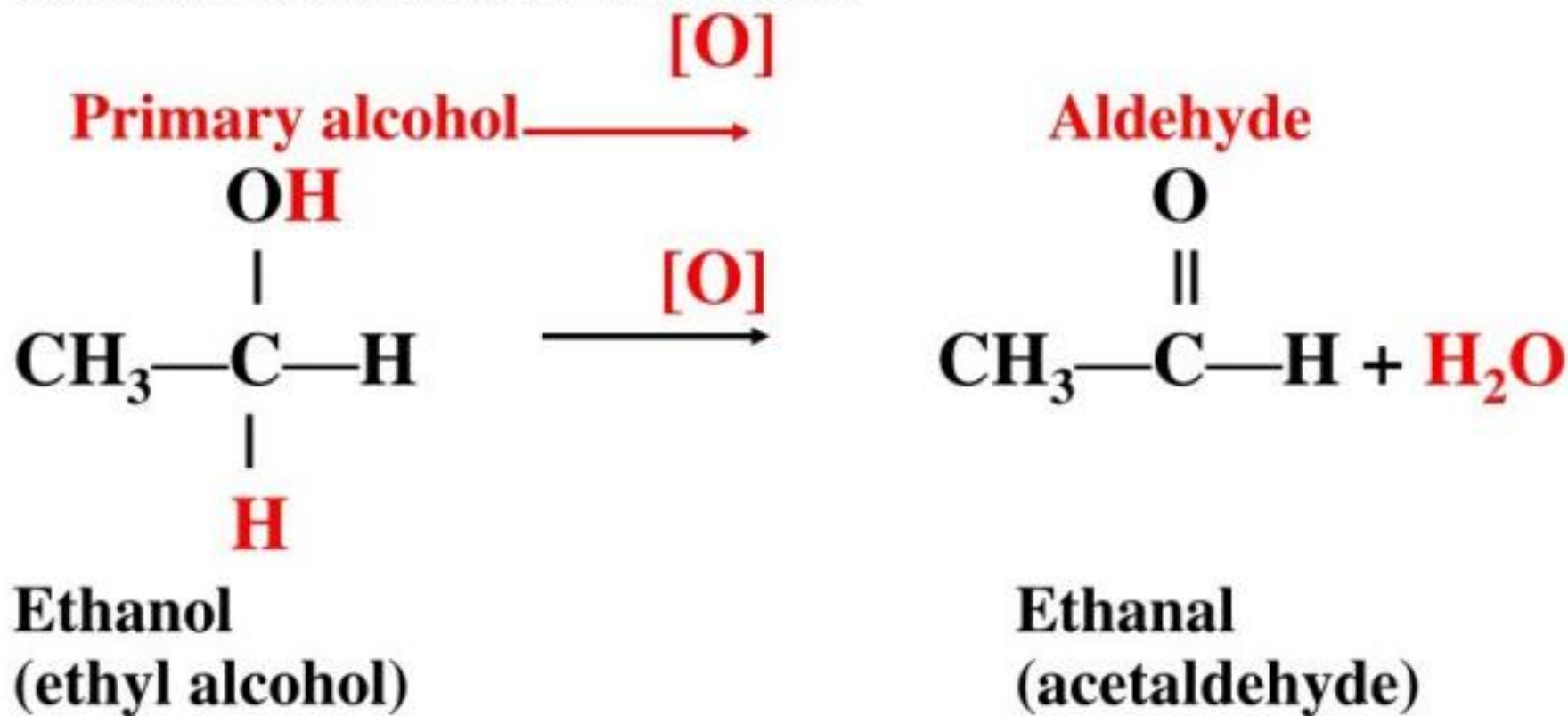
- In organic chemistry, **oxidation** is a loss of hydrogen atoms or a gain of oxygen.
- In an oxidation, there is an increase in the number of C-O bonds.
- **Reduction** is a gain of hydrogen or a loss of oxygen. The number of C-O bonds decreases.



Reactions of Alcohols

❖ Oxidation of Primary Alcohols

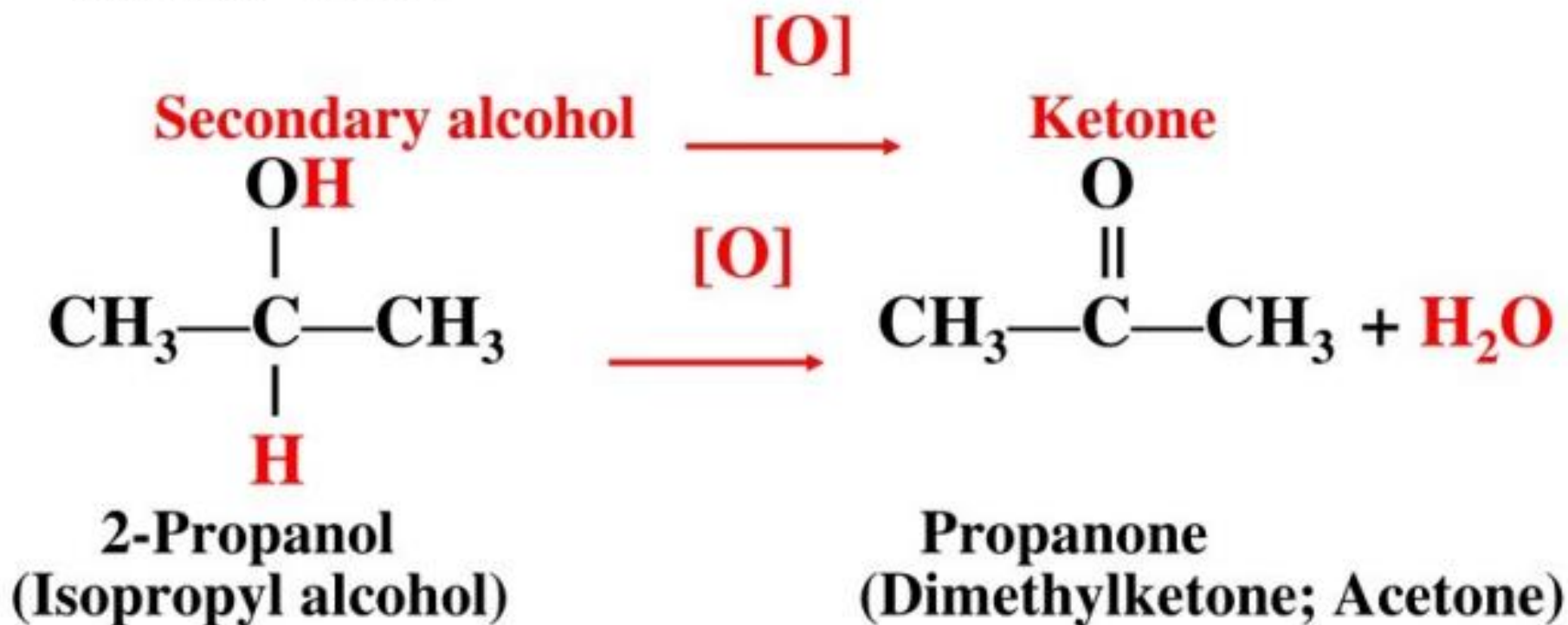
- In the oxidation [O] of a primary alcohol, one H is lost from the –OH and another H from the carbon bonded to the OH.



Reactions of Alcohols

❖ Oxidation of Secondary Alcohols

- The oxidation of a secondary alcohol removes one H from -OH and another H from the carbon bonded to the -OH .



Reactions of Alcohols

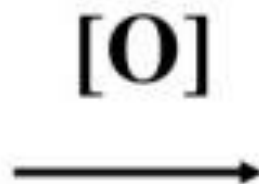
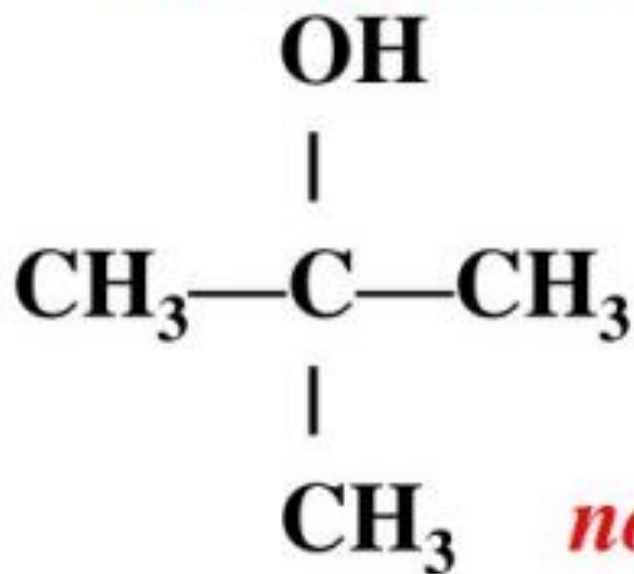
❖ Oxidation of Tertiary Alcohols

- Tertiary alcohols are resistant to oxidation.

Tertiary alcohols



no reaction



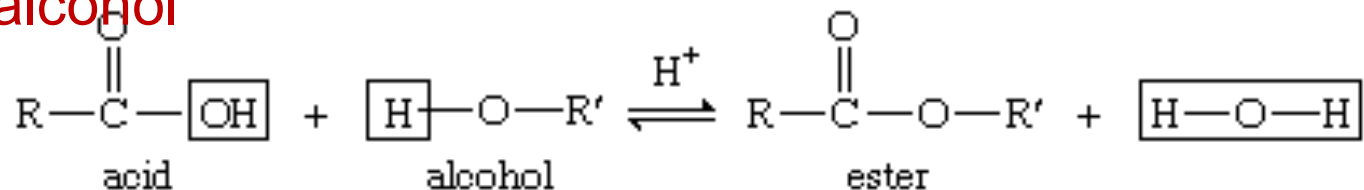
no product

2-Methyl-2-propanol

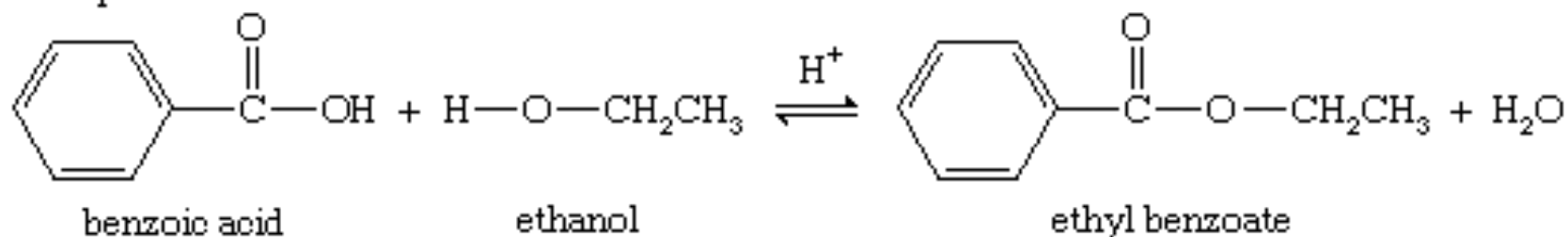
no H on the C-OH to oxidize

➤ ESTER FORMATION

This reaction Depend on the cleavage of bond between H and O In alcohol

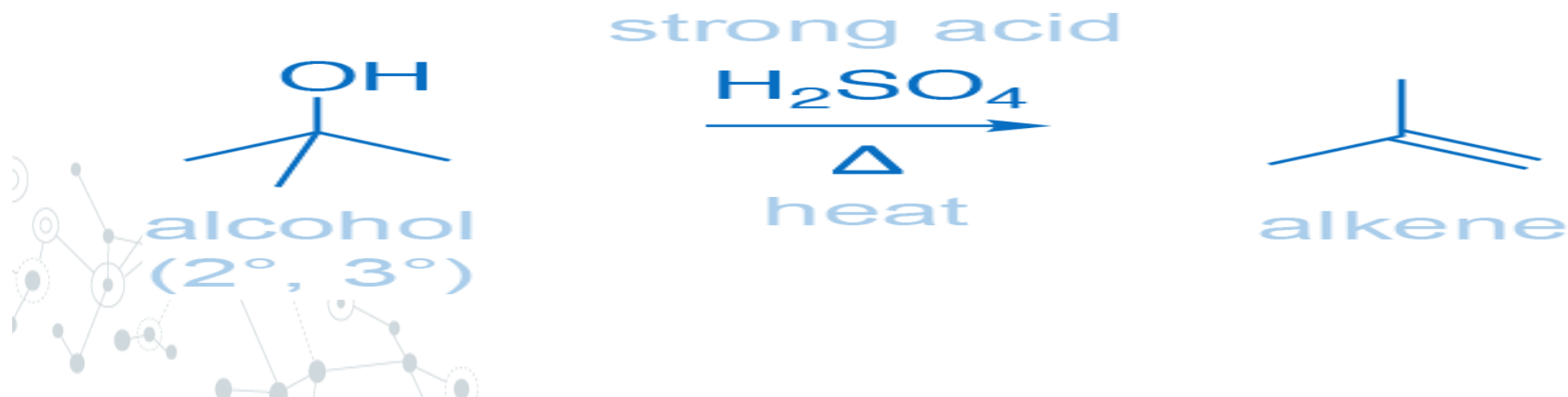


example:



➤ With strong acid (H₂SO₄) Elimination of water

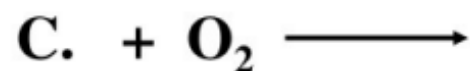
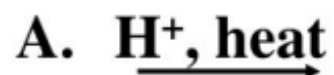
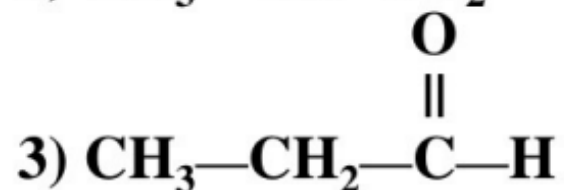
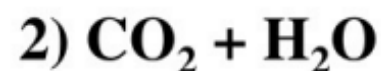
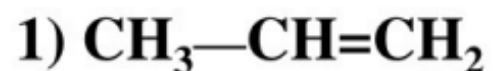
This reaction Depend on the cleavage of bond between OH and C In alcohol



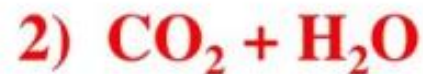
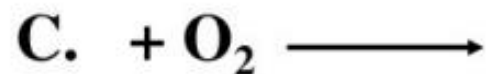
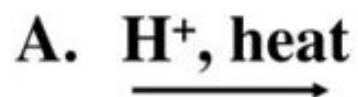
Reactions of Alcohols

❖ Exercise

Select the product for $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$.

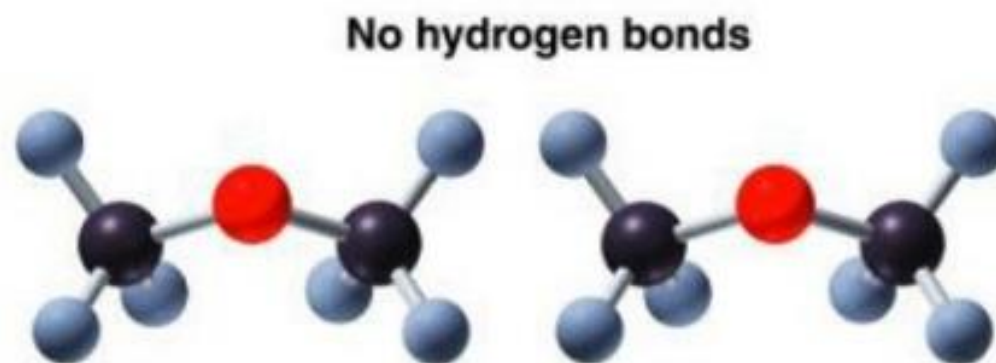


❖ Solution



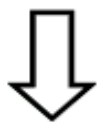
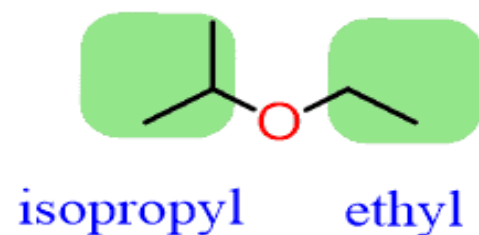
Ethers

- Ethers have an O atom, but there is no H attached.
- Thus, hydrogen bonds cannot form between ether molecules.

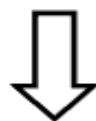
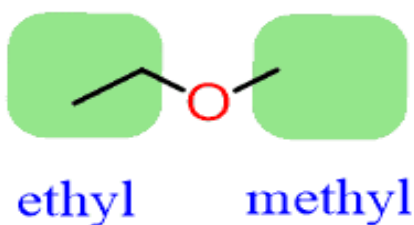


Dimethyl ether

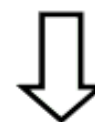
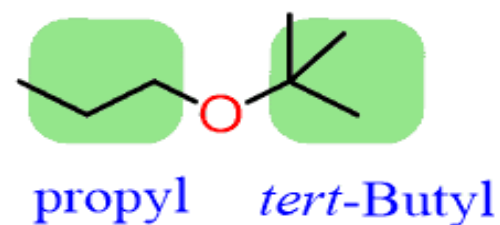
unsymmetrical ethers



Ethyl isopropyl ether

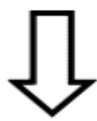
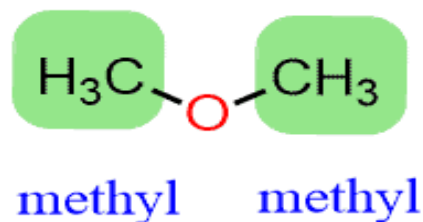


Ethyl methyl ether

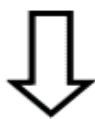
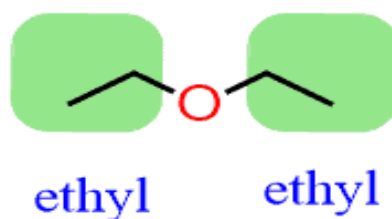


***tert*-Butyl propyl ether**

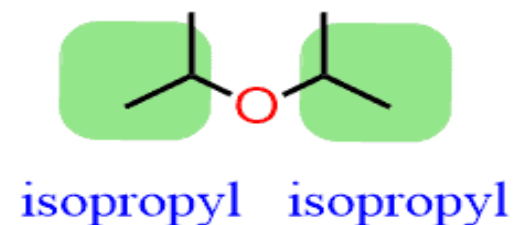
symmetrical ethers



Dimethyl ether



Diethyl ether



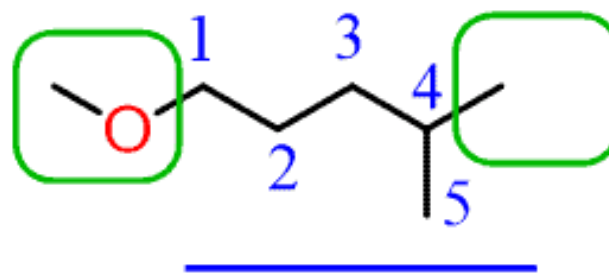
Diisopropyl ether

Naming Ethers by Systematic Nomenclature

- The alkoxy groups with shorter carbon chain is a substituent.
- The longest carbon chain is the parent chain.
- The substituents are placed alphabetically.



1-ethoxybutane

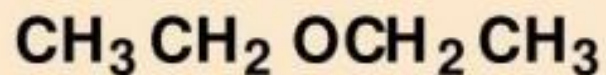


1-methoxy-4-methylpentane

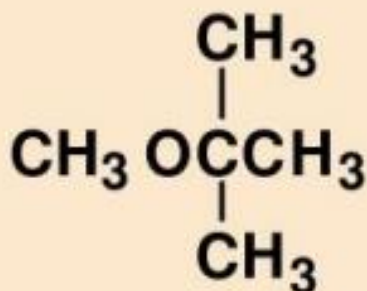
Ethers

❖ Nomenclature- Ethers

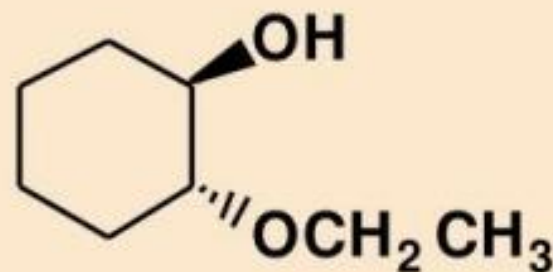
- **IUPAC:** the longest carbon chain is the parent. Name the OR group as an alkoxy substituent
- **Common names:** name the groups attached to oxygen followed by the word **ether**



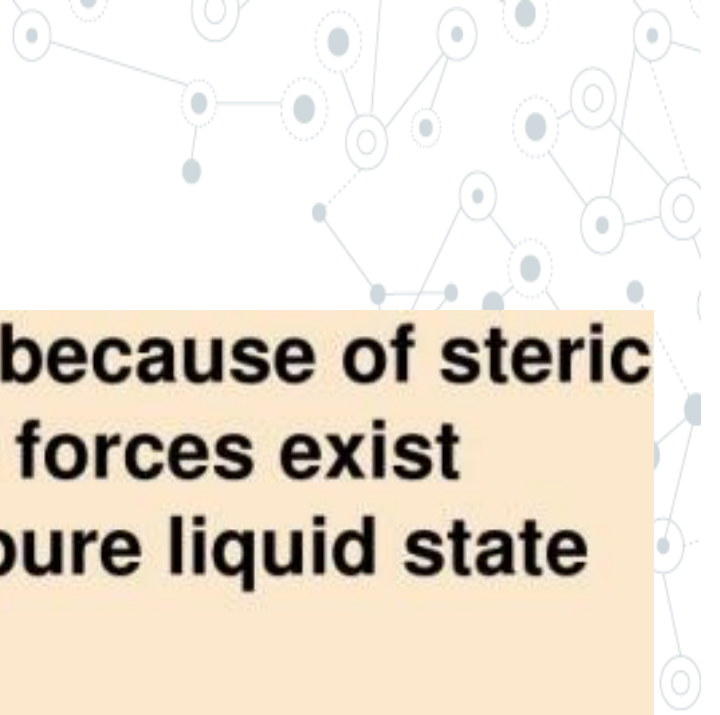
Ethoxyethane
(Diethyl ether)



2-Methoxy-2-methylpropane
(methyl *tert*-butyl ether, MTBE)



trans-2-Ethoxycyclohexanol



Ethers

❖ Physical prop.

- Ethers are polar molecules, but because of steric hindrance, only weak attractive forces exist between their molecules in the pure liquid state
 - Boiling points of ethers are
 - lower than alcohols of comparable MW and
 - close to those of hydrocarbons of comparable MW
 - Ethers hydrogen bond with H_2O and are more soluble in H_2O than are hydrocarbons
- 

Physical properties of ethers

- Molecules only slightly polar.
- No hydrogen on the oxygen atoms to form hydrogen bonds – only weak forces of attraction between molecules.
- Boiling points similar to corresponding alkane.
- Lower ethers, very volatile, highly flammable.
- Only slightly soluble in water, mix well with other non-polar solvents eg alkanes. (Like dissolves like).

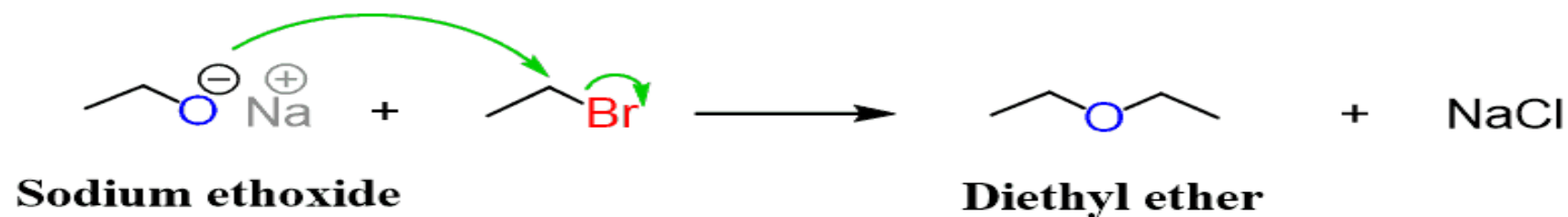
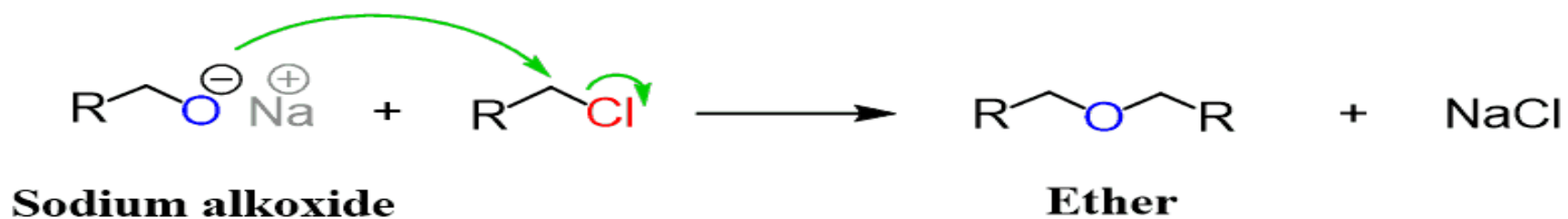
Ethers

❖ Reaction of Ethers

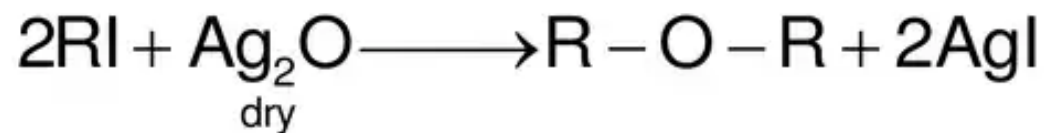
- **Ethers, $R-O-R$, resemble hydrocarbons in their resistance to chemical reaction**
 - they do not react with strong oxidizing agents such as chromic acid, H_2CrO_4
 - they are not affected by most acids and bases at moderate temperatures
- **Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out organic reactions**

Preparation

The Williamson Ether Synthesis



➤ From alkyl halides with dry silver oxide

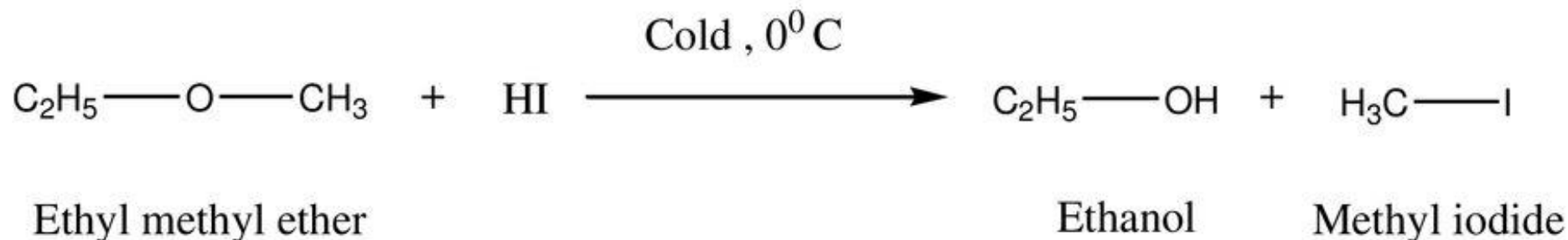
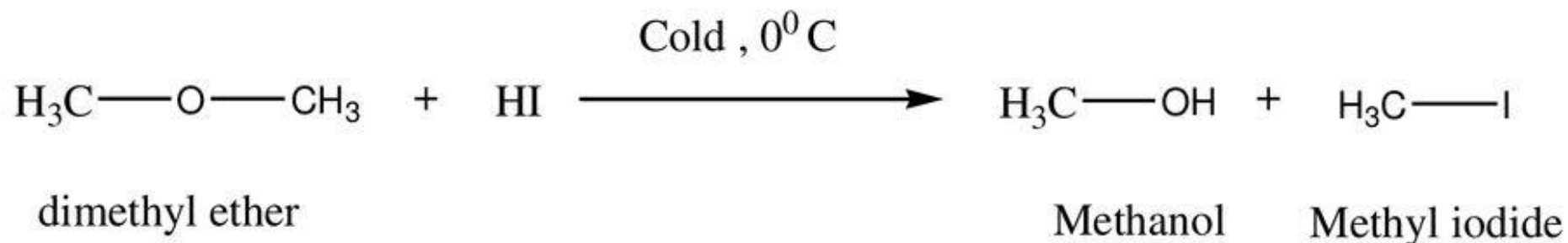


Reaction of ethers

1) Reaction with conc. HI :

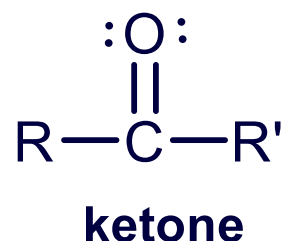
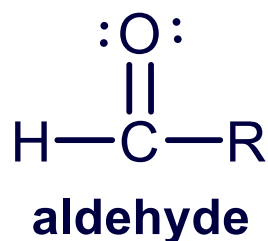
a) At cold condition: -

simple ether reacts with conc. HI in cold to give alcohol & alkyl iodide. In case of reaction of mixed ether higher alkyl group form alcohol.



Aldehydes and Ketones

- Aldehydes and ketones both contain the **carbonyl** group, $\text{C}=\text{O}$.

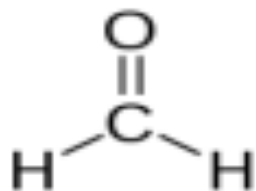


R and R' indicate hydrocarbon groups.

- Aldehydes are named by replacing the final *-e* of the alkane name with the **suffix -al**.
- Ketones have the **suffix -one** and the position of the carbonyl must always be indicated.

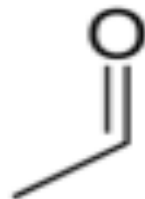
Aldehydes and Ketones

❖ Some common and IUPAC naming of aldehydes



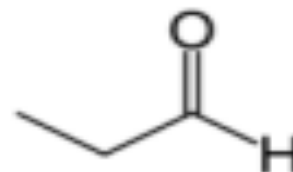
Common: Formaldehyde

IUPAC: Methanal



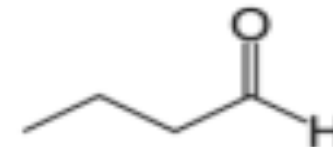
Common: Acetaldehyde

IUPAC: Ethanal



Common: Propionaldehyde

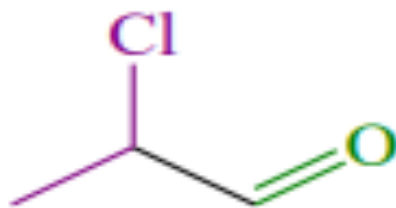
IUPAC: Propanal



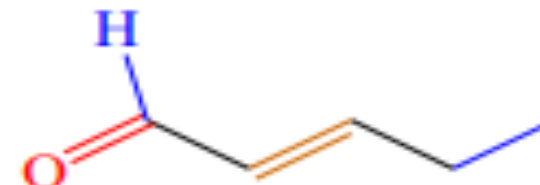
Common: Butyraldehyde

IUPAC: Butanal

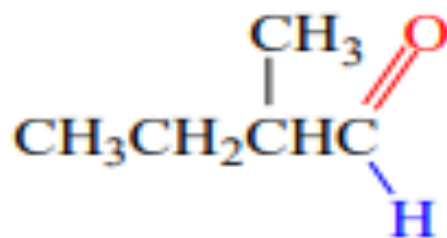
Examples



2-chloropropanal



2-pentenal



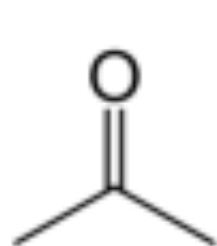
2-Methyl butanal



3-hydroxypropanal

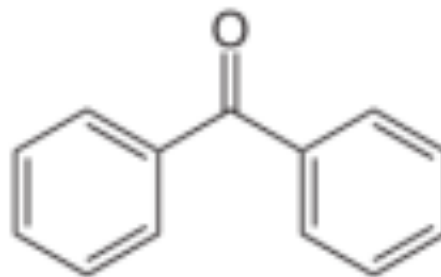
Aldehydes and Ketones

❖ Some common and IUPAC naming of ketones



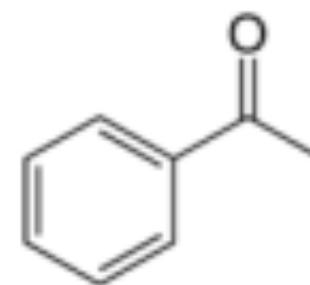
Common: Dimethylketone
acetone

IUPAC: Propanone



Common: Diphenylketone
Benzophenone

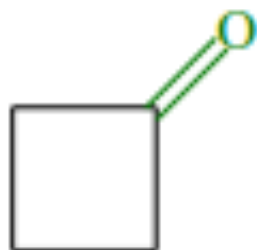
IUPAC: diphenylmethanone



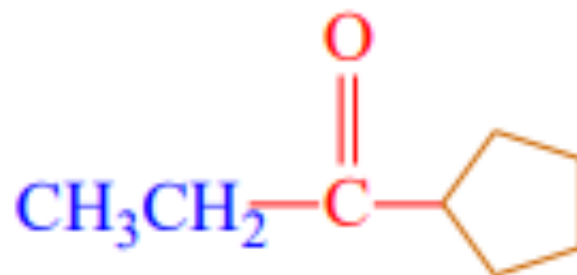
Common: Methylphenylketone
acetophenone

IUPAC: 1-phenylethanone

Examples:

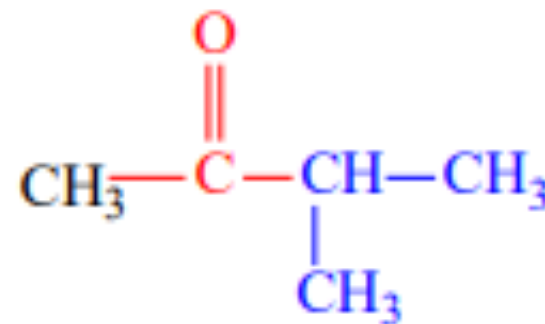


Common: Cyclobutanone



Common: Ethylcyclopentylketone

IUPAC: 1-Cyclopentyl propanone

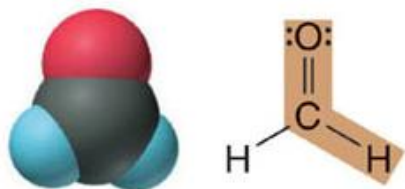


Common: Methyl isopropylketone

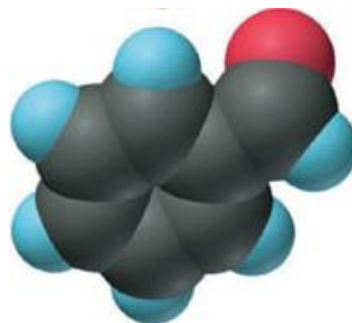
IUPAC: 3-Methylbutan-2-one

Aldehydes and Ketones

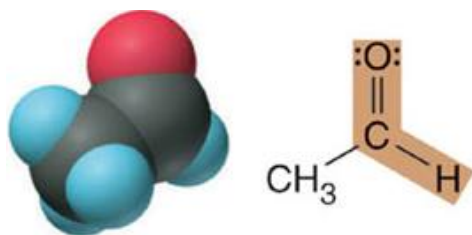
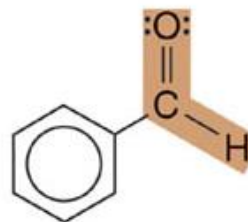
❖ Some common aldehydes and ketones.



Methanal (formaldehyde) Used to make resins in plywood, dishware, countertops; biological preservative



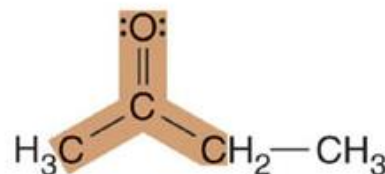
Benzaldehyde
Artificial almond flavoring



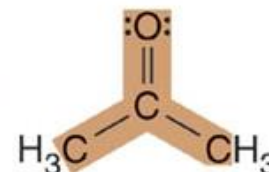
Ethanal (acetaldehyde)
Narcotic product of ethanol metabolism; used to make perfumes, flavors, plastics, other chemicals



2-Propanone (acetone)
Solvent for fat, rubber, plastic, varnish, lacquer; chemical feedstock

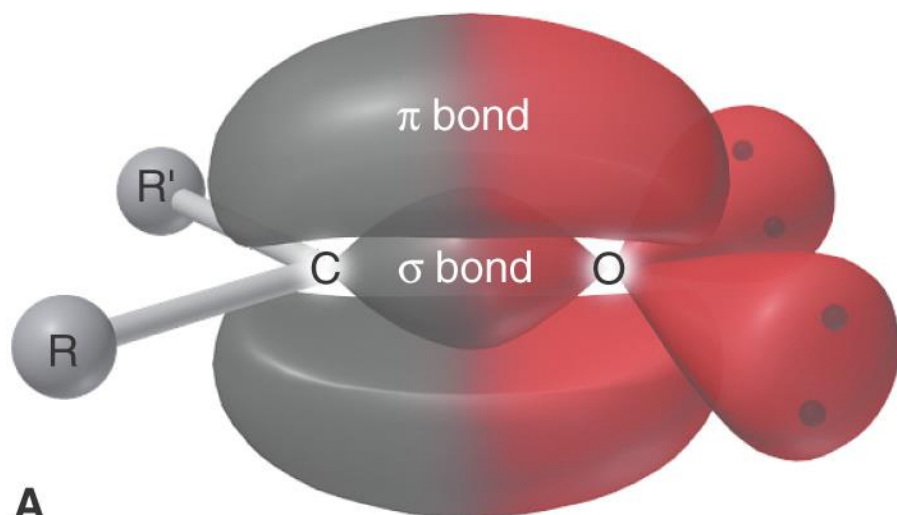


2-Butanone (methyl ethyl ketone)
Important solvent

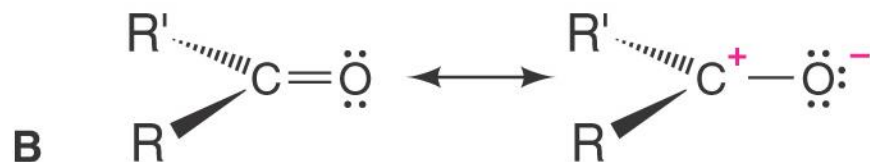


Aldehydes and Ketones

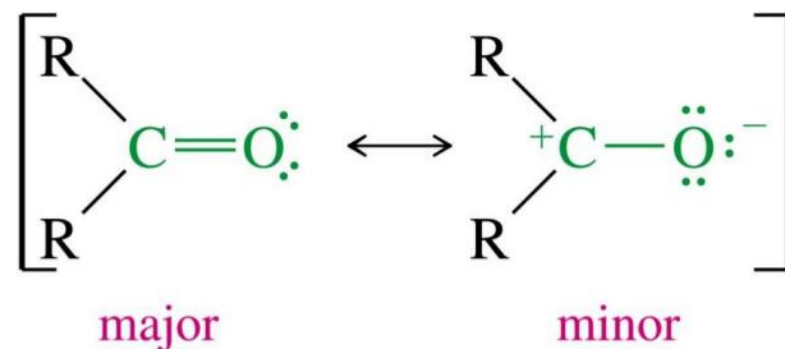
❖ The polar carbonyl group.



A



B



- The C=O bond is **electron rich** and is also **highly polar**. It readily undergoes **addition** reactions, and the electron-poor C atom attracts electron-rich groups.

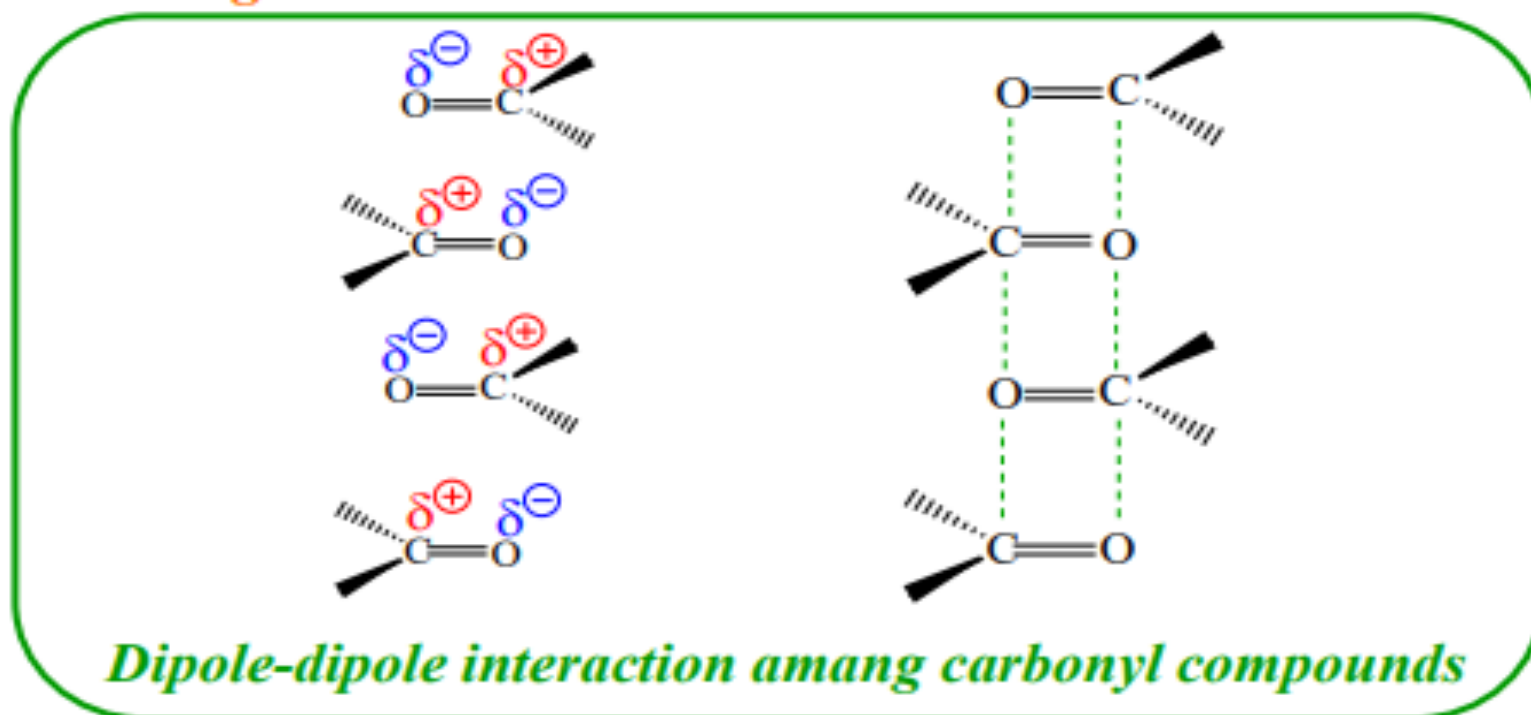
Aldehydes and Ketones

Physical Properties of Aldehydes and Ketones

A. Boiling Points

Because of polarity of carbonyl groups, aldehydes and ketones are polar compounds.

Dipole-dipole attractions, although important, are **not as strong as** interactions due to *hydrogen bonding*.

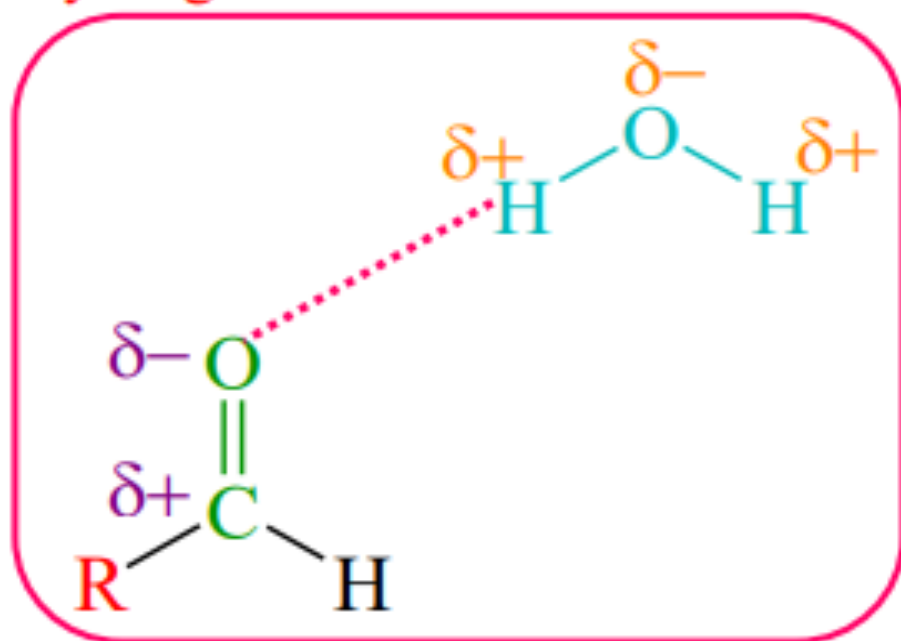


As a result, the boiling points of aldehydes and ketones are higher than those of nonpolar alkanes, but lower than those of alcohols.

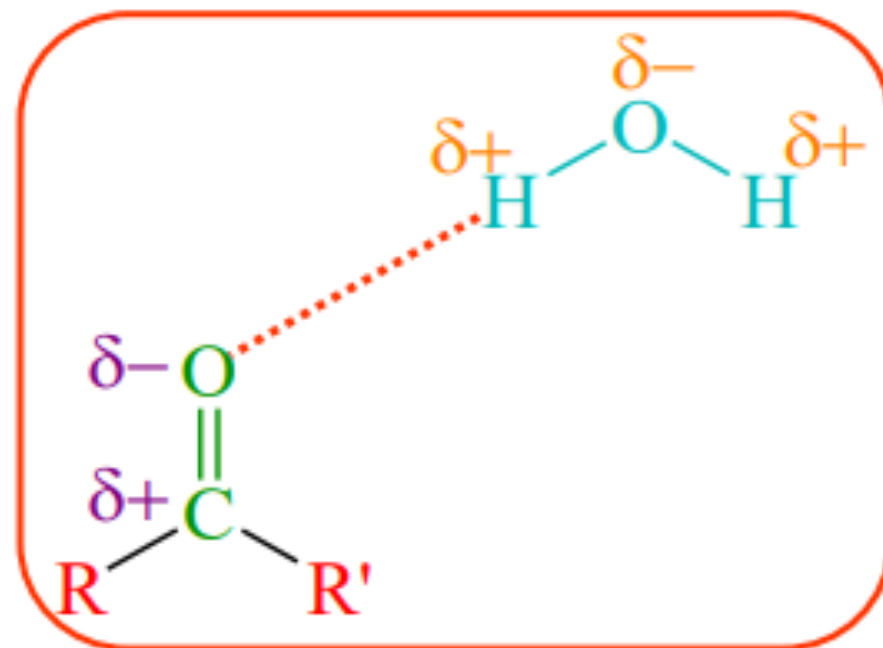
Aldehydes and Ketones

B. Solubility in water

The lower aldehydes and ketones are soluble in water because they form hydrogen bonds with water.



Intermolecular hydrogen bonding between water and aldehydes



Intermolecular hydrogen bonding between water and ketones.

- Aldehydes and ketones with less than six carbons are essentially **insoluble** in water.
- The higher aldehydes and ketones are soluble in organic solvents such as; benzene, ether, and carbontetrachlorid.

Aldehydes and Ketones

Preparation of Aldehydes and Ketones

The major methods for preparing aldehydes and ketones are:

1. Oxidation of alcohols

2. Ozonolysis of alkenes.

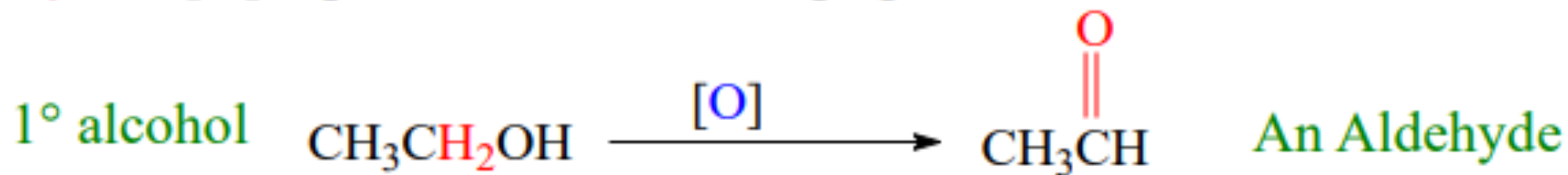
3. Hydration of alkynes

4. Friedel-Crafts acylation

Aldehydes and Ketones

1. Oxidation of alcohols

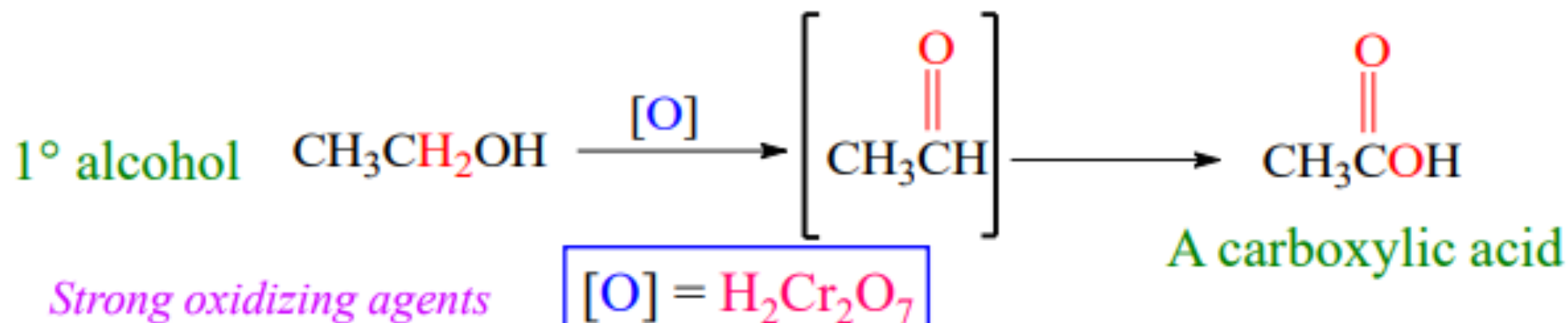
✓ The oxidation of *primary alcohols*, using **mild oxidizing agents** yields **aldehydes**. [O] represents the oxidizing agent used.



Mild oxidizing agent



✓ When **strong oxidizing agents** are used, the **aldehydes** are very easily oxidized to further **carboxylic acids**.

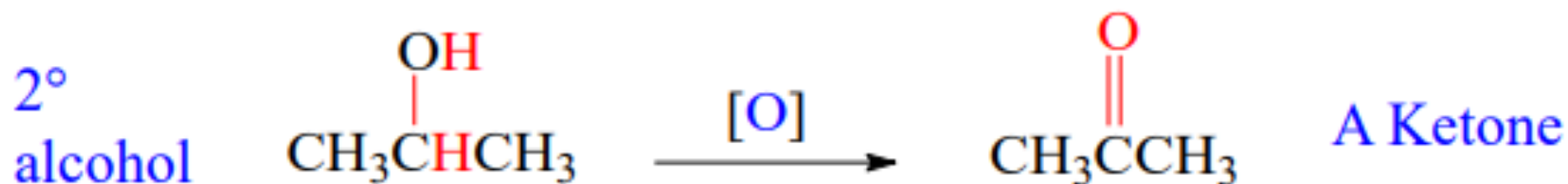


Strong oxidizing agents



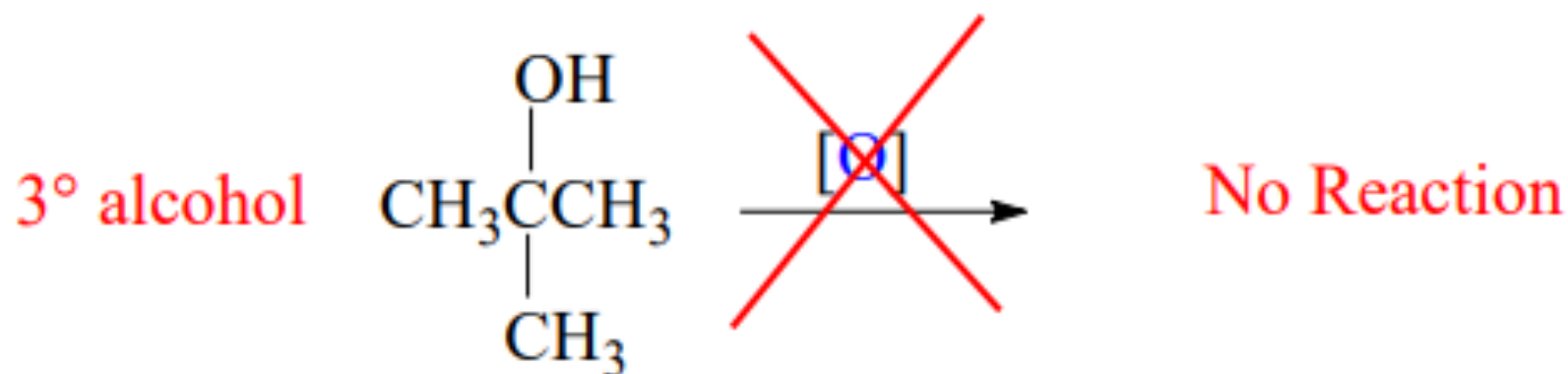
Aldehydes and Ketones

✓ *Secondary alcohols*, are converted either into *ketones* on treatment with both **mild** or **strong** oxidizing agent.



[O] = may be CrO_3 / pyridine ; Cu/ heat or $\text{H}_2\text{Cr}_2\text{O}_7$

✓ For oxidizing a *tertiary alcohol*, Nothing happens.



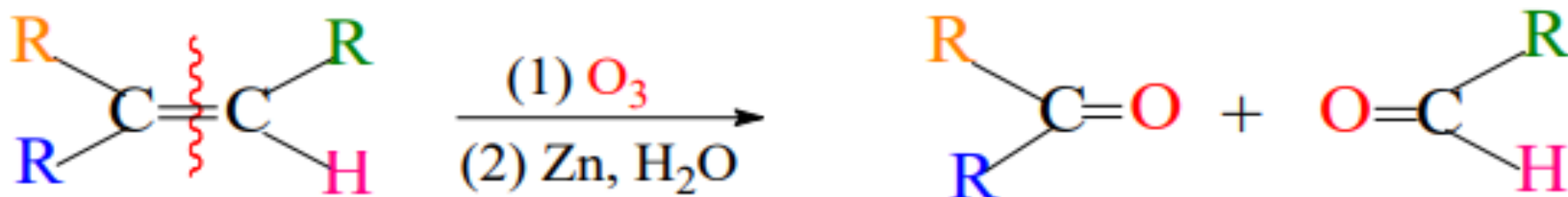
✓ This reaction also illustrates the importance of **differentiating** between **primary**, **secondary**, and **tertiary** alcohols.

Aldehydes and Ketones

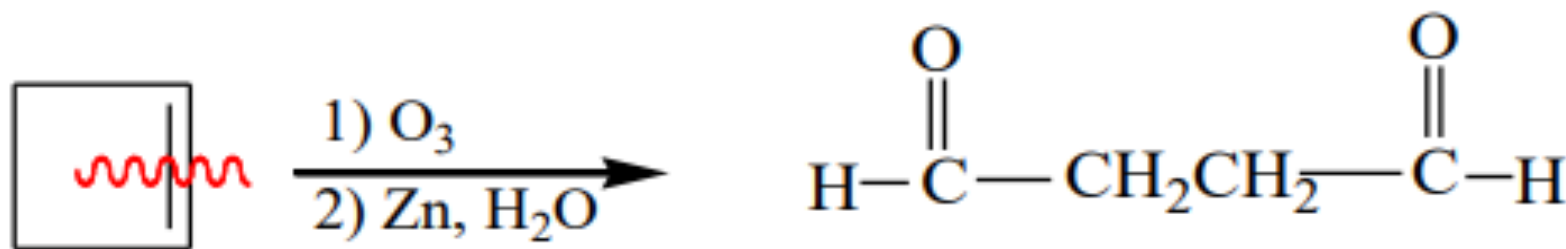
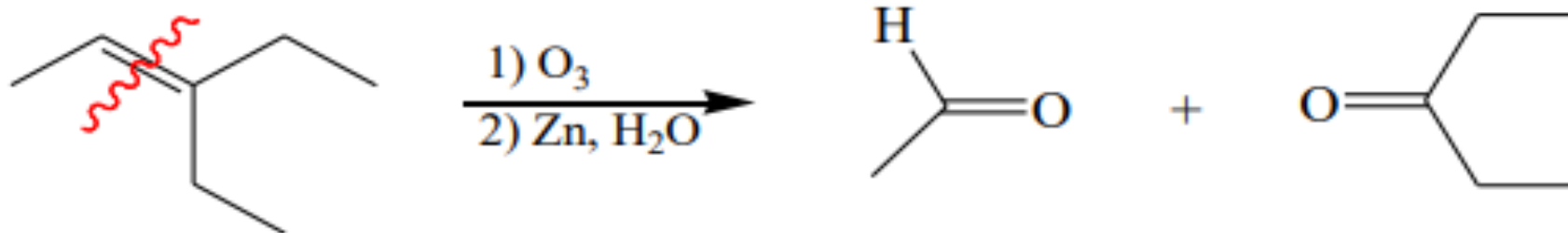
2. Ozonolysis of alkenes

Results in **aldehydes** or **ketones** depending on structure of **the alkene** used.

General equation



Examples

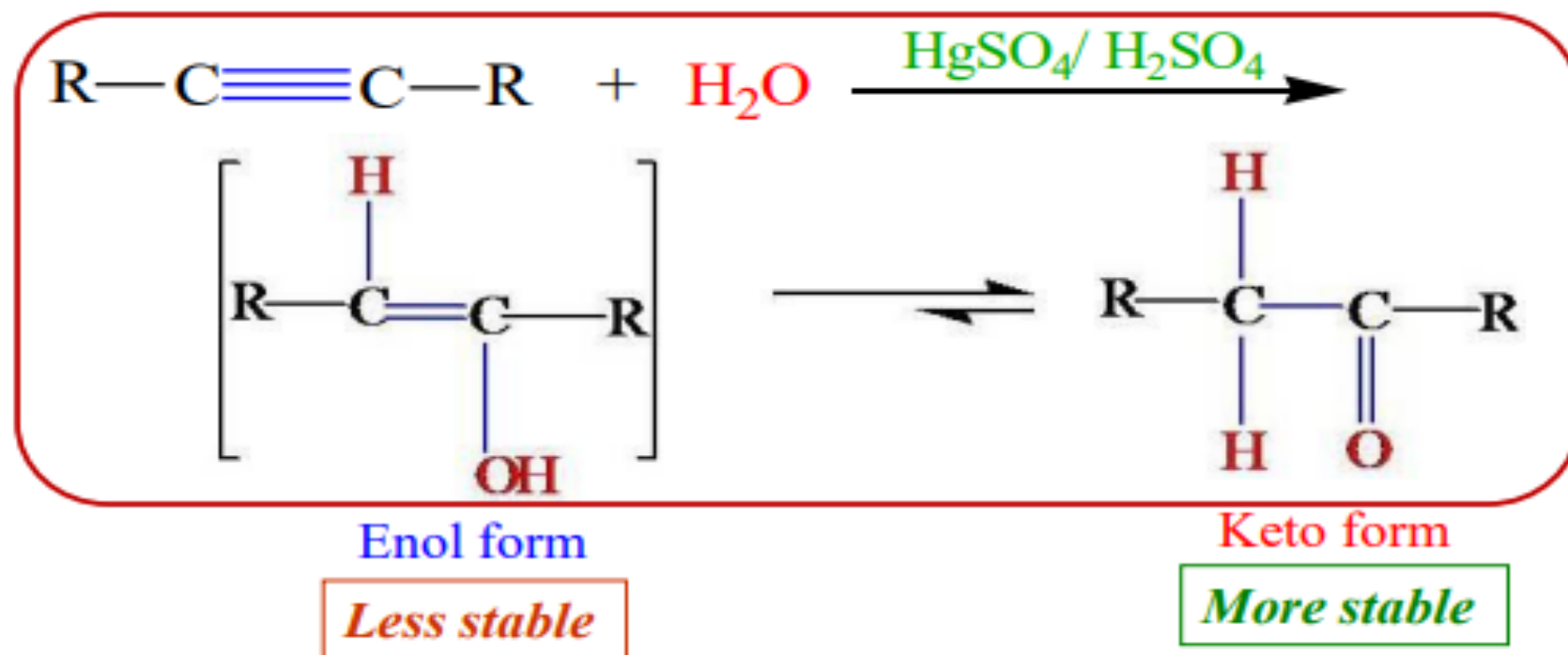


Aldehydes and Ketones

3. Hydration of alkynes: Addition of water

Water adds to alkynes in the presence of dilute sulfuric acid and mercuric sulfate catalyst, to yield an enol. However the initially formed enol reacts further to produce a ketone.

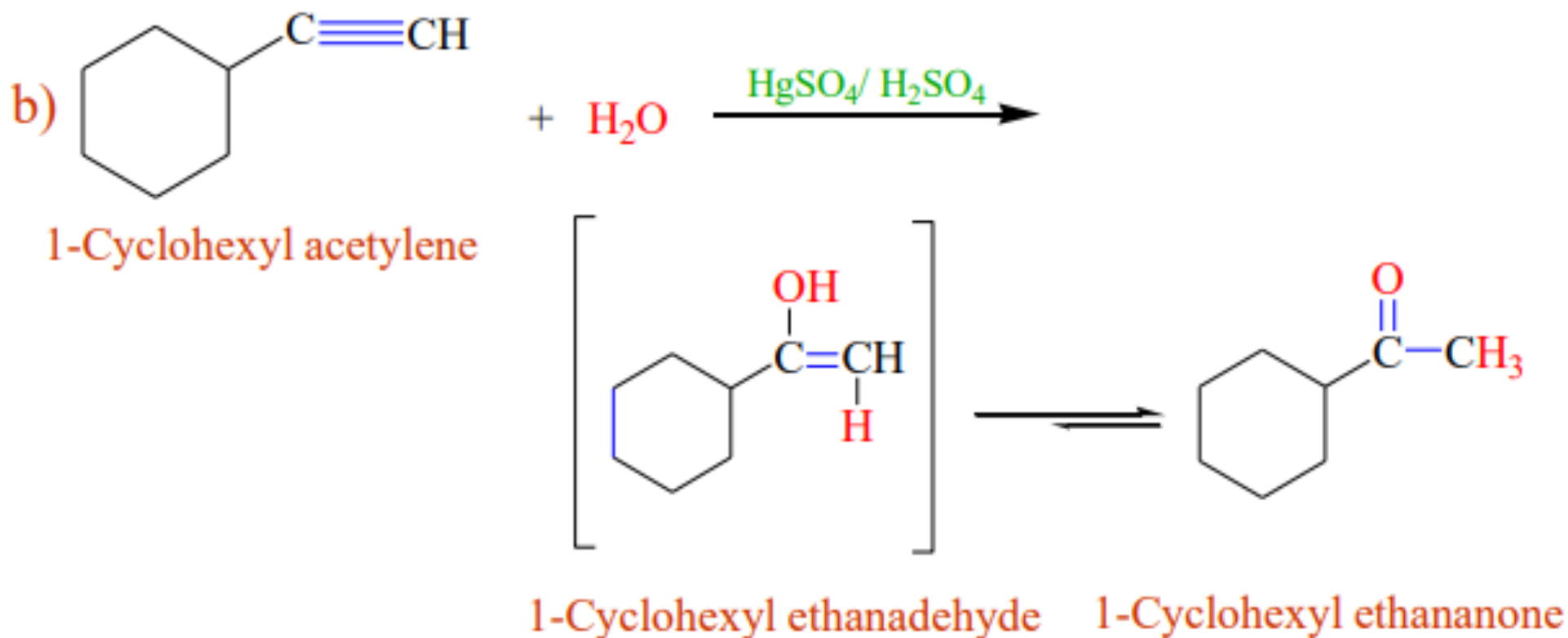
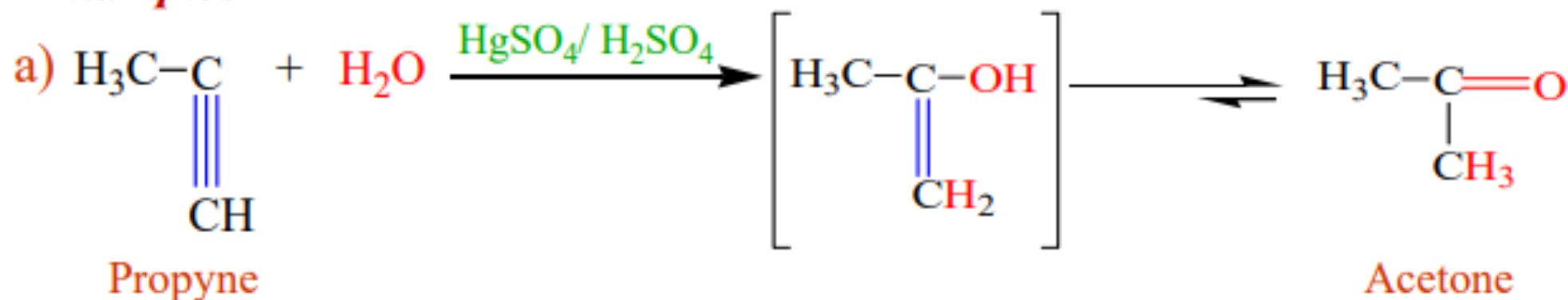
General equation



✓ Such isomers, differing only in the placement of a hydrogen atom, are called **tautomers**.

Aldehydes and Ketones

Examples

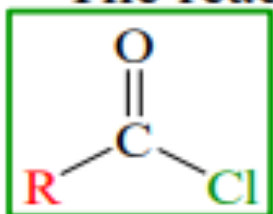


Aldehydes and Ketones

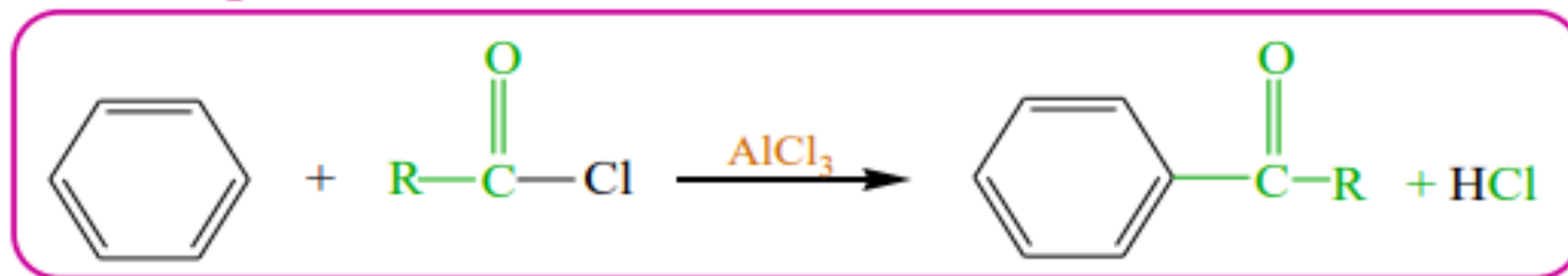
4- Friedel-Crafts acylation

A general method for preparing **ketones** that contain an **aromatic ring** is the **Friedel-Crafts acylation** reaction.

The reaction involves treatment of an **aromatic ring** with an **acylchloride**, in the presence of AlCl_3 , which acts as a **catalyst**.



General equation



Examples



Propionyl chloride

Ethyl phenyl ketone

Propiophenone

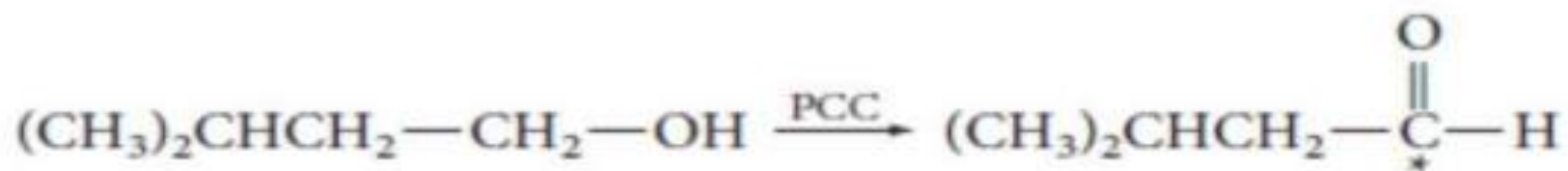
Aldehydes and Ketones

EXAMPLE:

Write an equation for the oxidation of an appropriate alcohol to $(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$ (3-methylbutanal).

Solution :

Aldehydes are prepared by oxidation of 1° alcohols (RCH_2OH) with an oxidizing agent(PCC) .First, find the carbonyl carbon in 3-methylbutanal .Convert this carbon to a primary alcohol. A proper equation is:



Aldehydes and Ketones

Reactions of Aldehydes and Ketones

Aldehydes and ketones undergo *nucleophilic addition reaction* to the carbon-oxygen double bond.

1. Addition of metal hydrides: *Formation of alcohols.*
2. Addition of Grignard Reagents : *Formation of alcohols.*
- 3-Oxidations of aldehydes and ketones:

a.Oxidation under acidic conditions/ H^+

b. Under alkaline conditions/ OH^-

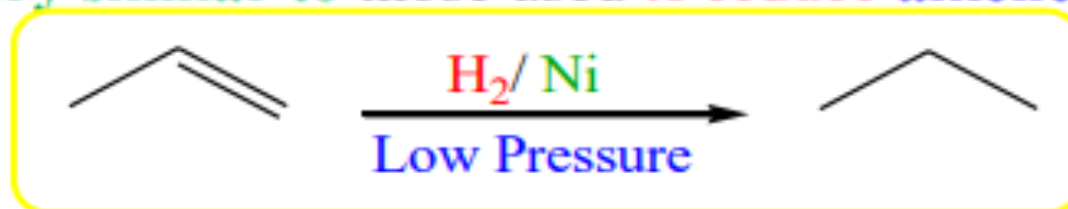
4. Tollen's Test: Silver mirror test.
5. Addition of Hydrogen cyanide: *Formation of cyanohydrin.*
- 6- Nucleophilic addition of Acetylide ions:
- 7- Nucleophilic Addition of Alcohols:
Formation of Hemiacetals and Acetals.
- 8- Addition of Ammonia and Ammonia Derivatives.
- 9- Aldol condensation reaction.
- 10 - Cannizzaro reaction.

Aldehydes and Ketones

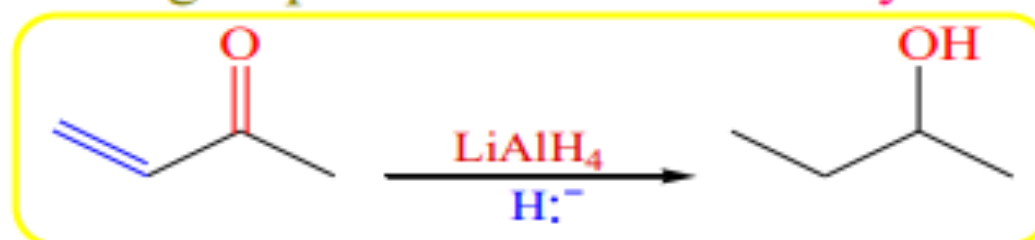
1. Addition of metal hydrides: Formation of alcohols.

Metal Hydrides; LiAlH_4 , NaBH_4

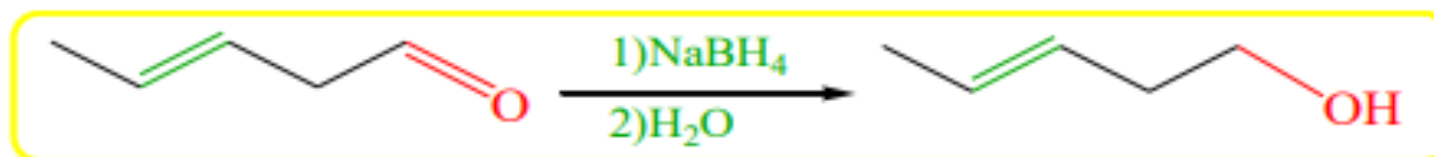
💡 Catalytic hydrogenation reduces aldehydes to produce 1° alcohols & ketones to produce 2° alcohols.
(conditions are **very similar to** those used to reduce alkene double bonds).



💡 Lithium aluminum hydride; LiAlH_4 is a very strong reducing agent that will reduce many functional groups in **addition to aldehydes** and **ketones**.



💡 Sodium borohydride; NaBH_4 is a much weaker reducing agent that basically will **reduce only aldehydes** and **ketones** to alcohols.

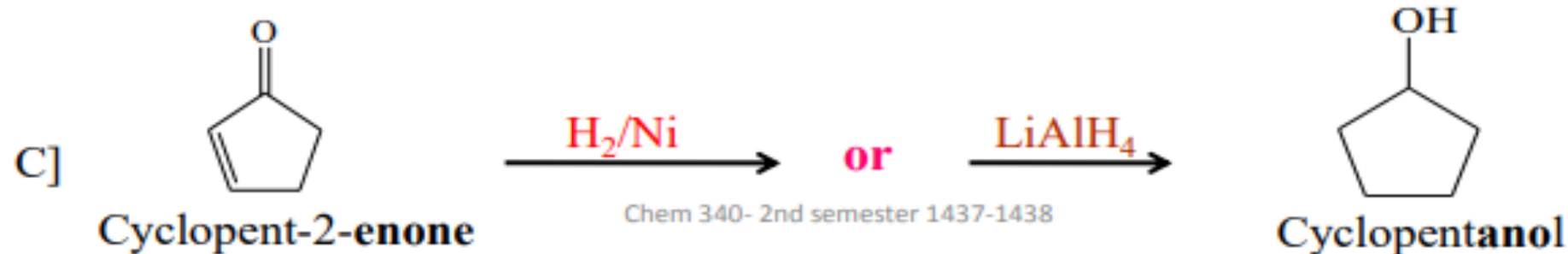
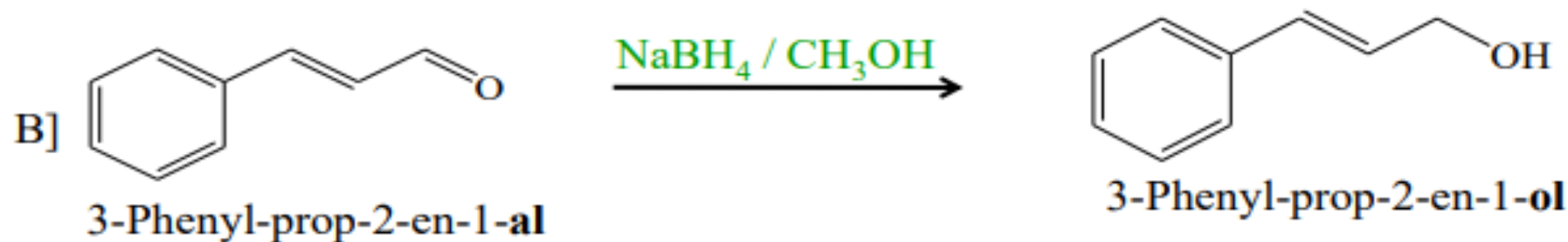
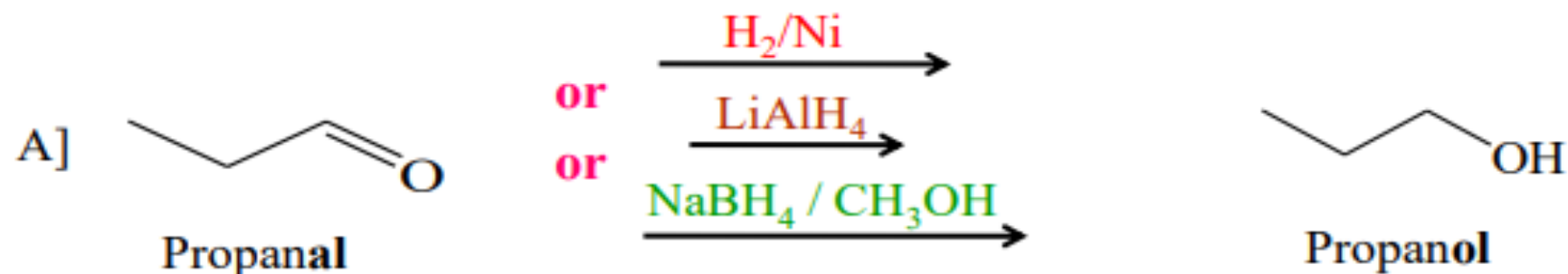


Aldehydes and Ketones

Conclusion

Although the same result may be achieved by **catalytic hydrogenation**, or **LiAlH_4** , but **NaBH_4** has *the advantage of selectively* reducing of unsaturated **aldehydes** and **ketones** into unsaturated **alcohols**.

Exercise: Choose the best reagent for the following reactions.



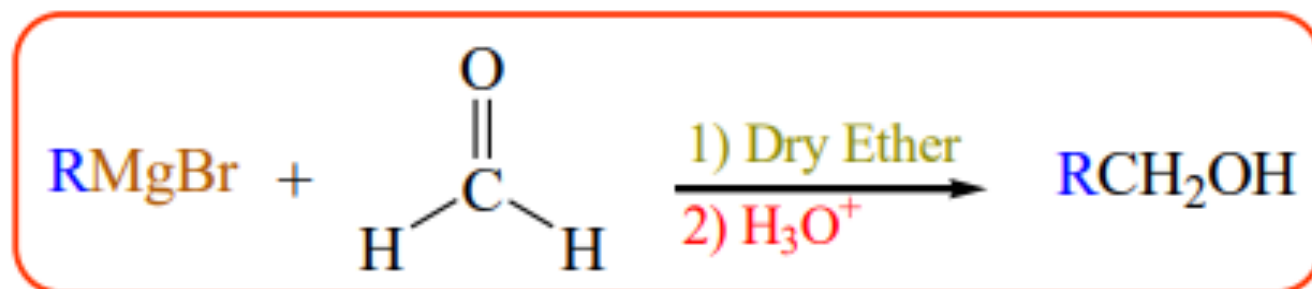
Aldehydes and Ketones

2. Addition of Grignard Reagents : Formation of alcohols.

- ✓ Grignard reagents are strong nucleophiles that they can serve as nucleophilic addition to carbonyl group.
- ✓ Treatment of an aldehyde or ketone with Grignard reagent followed by water forms an alcohol with new C-C bond.

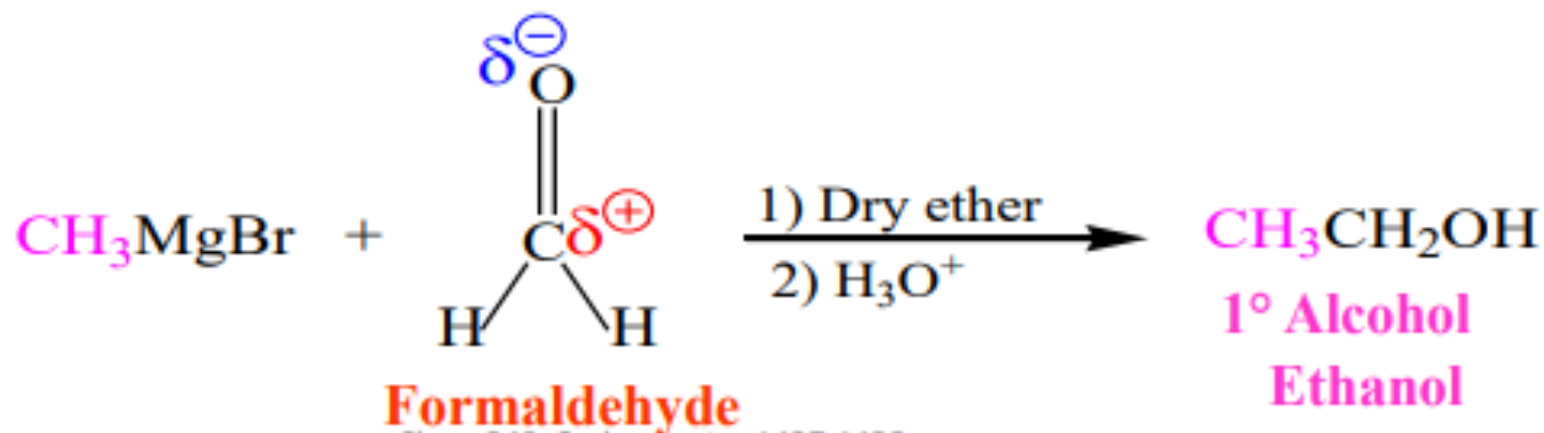
General equation

1. In case of formaldehyde:



Grignard reagents react with *formaldehyde* to produce **primary alcohols**.

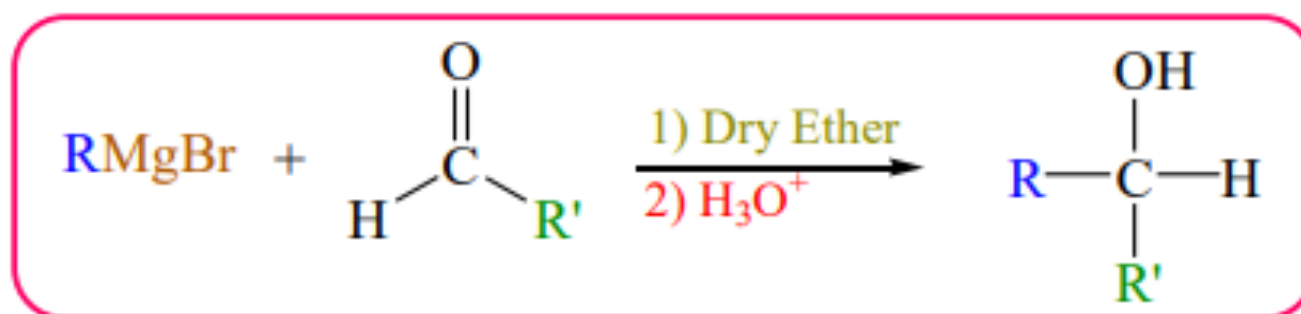
Example:



Aldehydes and Ketones

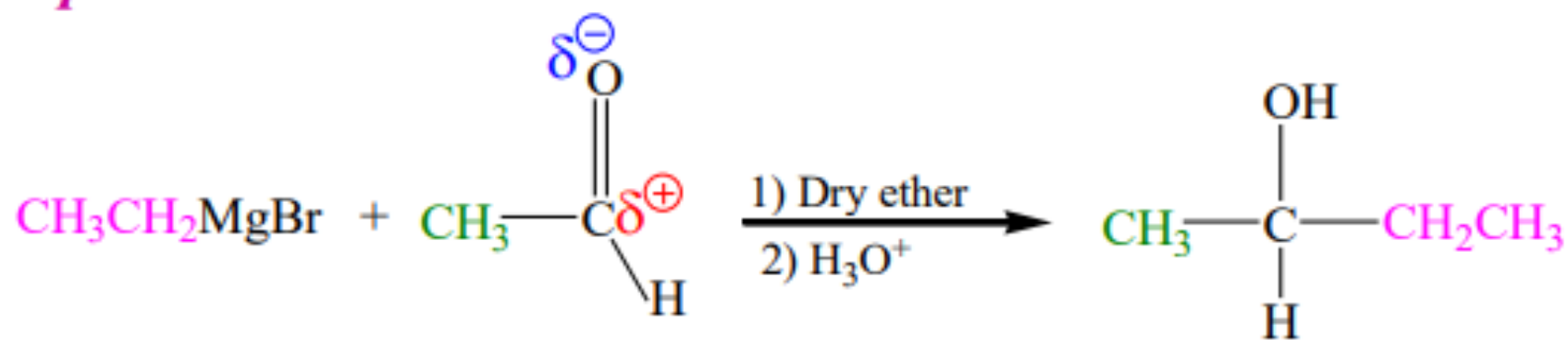
2. In case of *other aldehyde*:

General equation



✓ Grignard reagents react with *aldehyde* to produce *secondary alcohols*.

Examples:



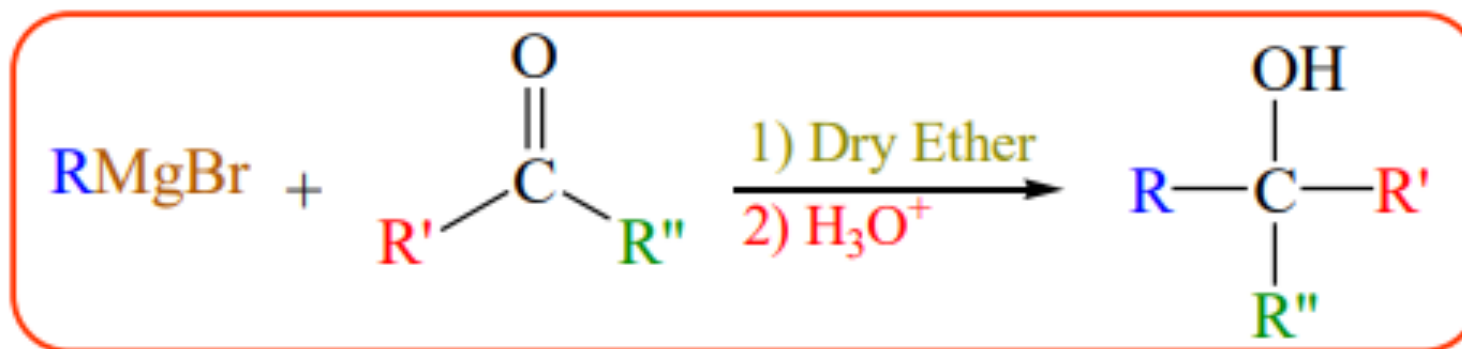
Aldehyde
Acetaldehyde

2° Alcohol
2-Butanol

Aldehydes and Ketones

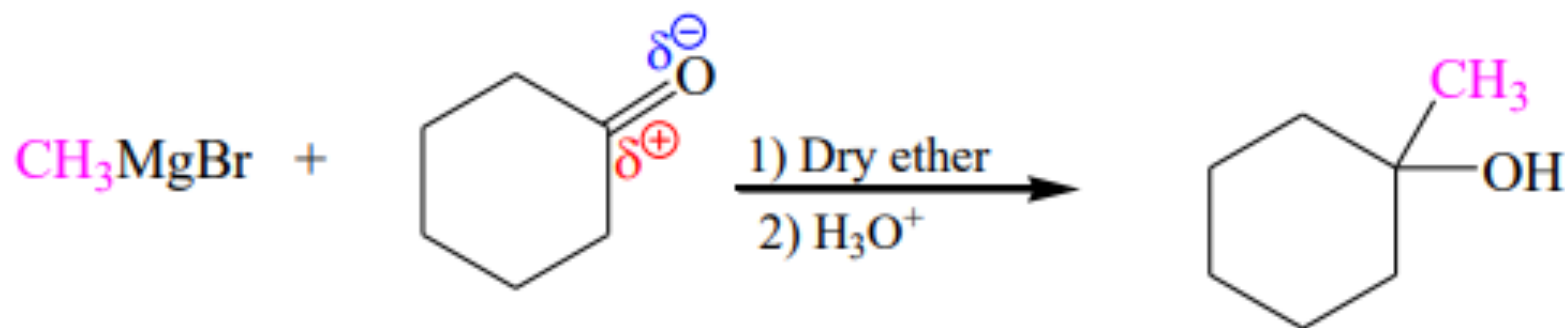
General equation

3. In case of Ketones:



✓ Grignard reagents react with *ketones* to produce *tertiary alcohols*.

Examples:



ketones

cyclohexanone

3° Alcohol

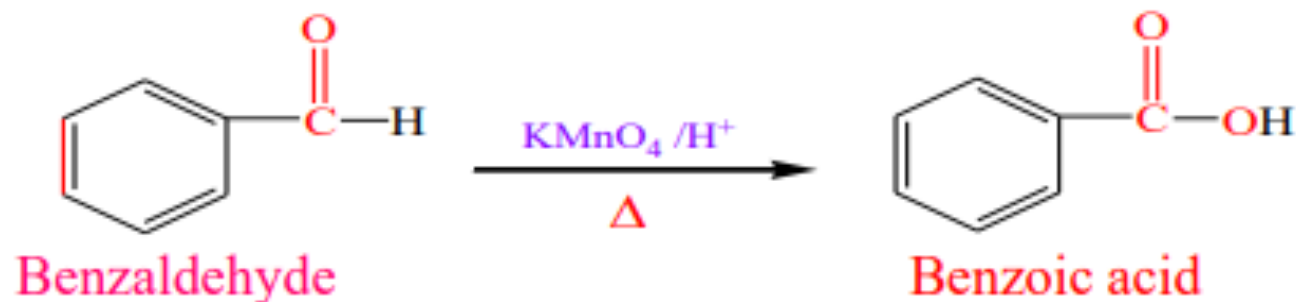
cyclohexyl methyl alcohol

Aldehydes and Ketones

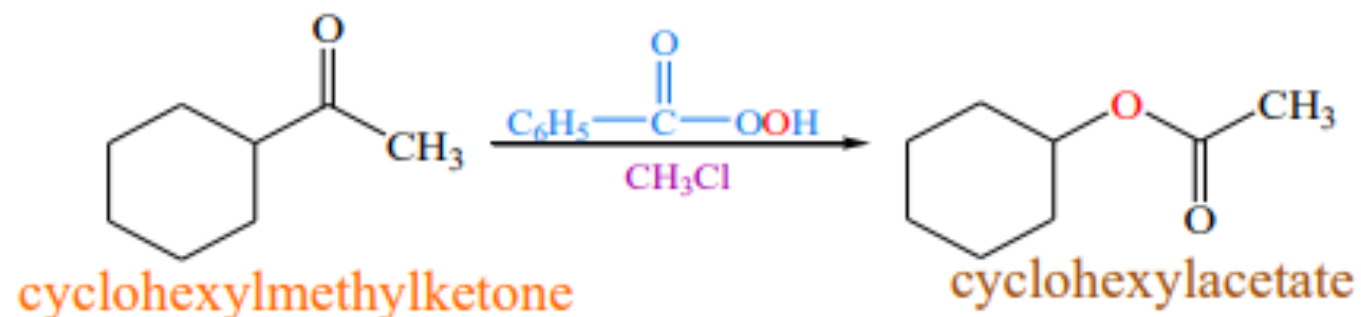
3-Oxidations of aldehydes and ketones

a. Oxidation under acidic conditions/ H^+

- ✓ Aldehydes can be oxidized to carboxylic acid with both mild and strong oxidizing agents.
- ✓ Typical oxidizing agents for aldehydes include either potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$) in acid solution.



- ✓ Peroxy acids, such as peroxybenzoic acid ($C_6H_5CO_3H$) are used to oxidize ketones to esters.

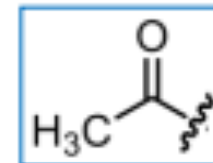



Oxygen insertion
occurs between
carbonyl carbon
and larger group.

Aldehydes and Ketones

The iodoform test

b. Under alkaline conditions/ OH^-



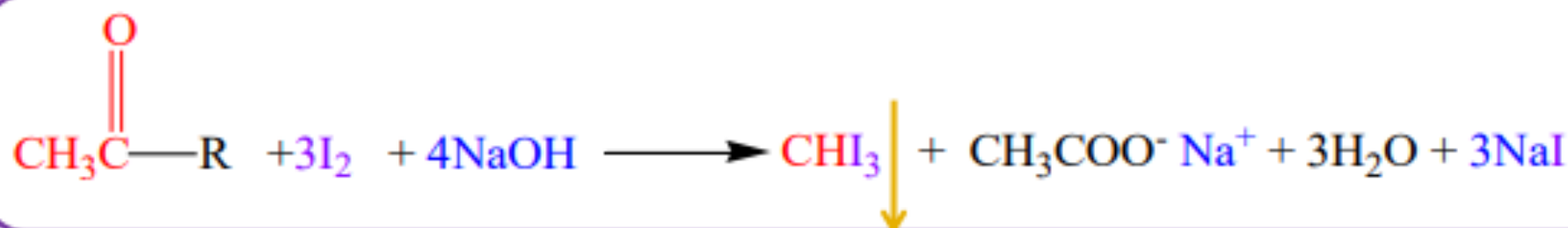
or

✓ The iodoform test is a test for the existence an acetyl group, a group that can be oxidized to an acetyl group which will give a positive iodoform test.

✓ The compounds containing $\text{CH}_3\text{C}(=\text{O})\text{—}$ or $\text{CH}_3\text{CH}(\text{OH})\text{—}$, give iodoform test.

✓ These type of methylketones can be distinguished from other non-methyl ketone by their reaction with iodine; I_2 in a basic solution; NaOH to yield iodoform (CHI_3) as a yellow colored precipitate.

The General equation



iodoform, yellow ppt

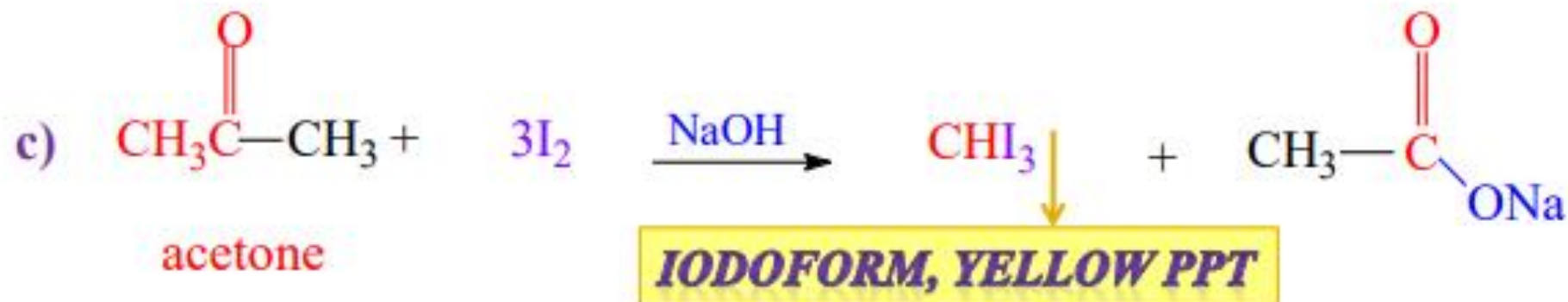
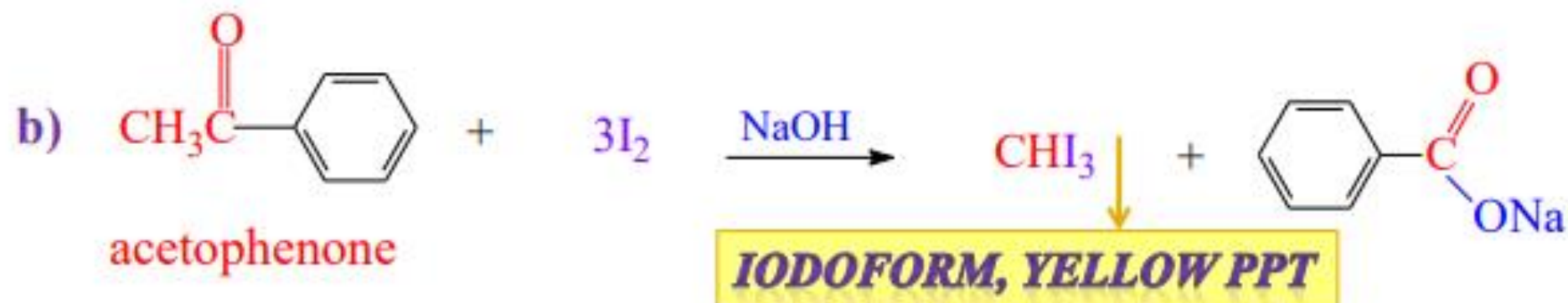
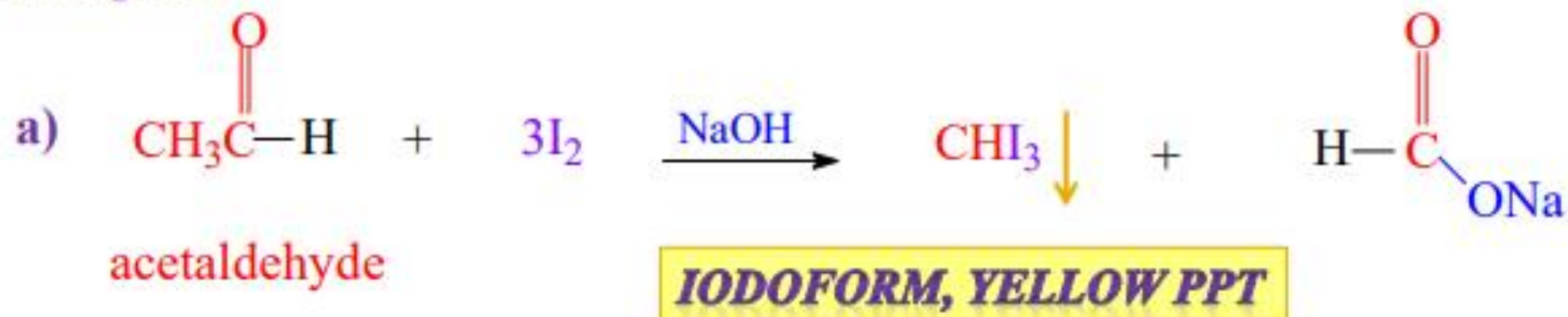
-ve
Iodoform



+ve Iodoform(CHI_3) result =
is a pale yellow substance.

Aldehydes and Ketones

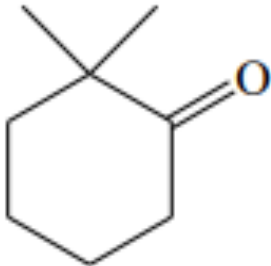
Examples:



Aldehydes and Ketones

Exercise:

Which of the following compounds will give a positive result +ve toward *iodoform* test:

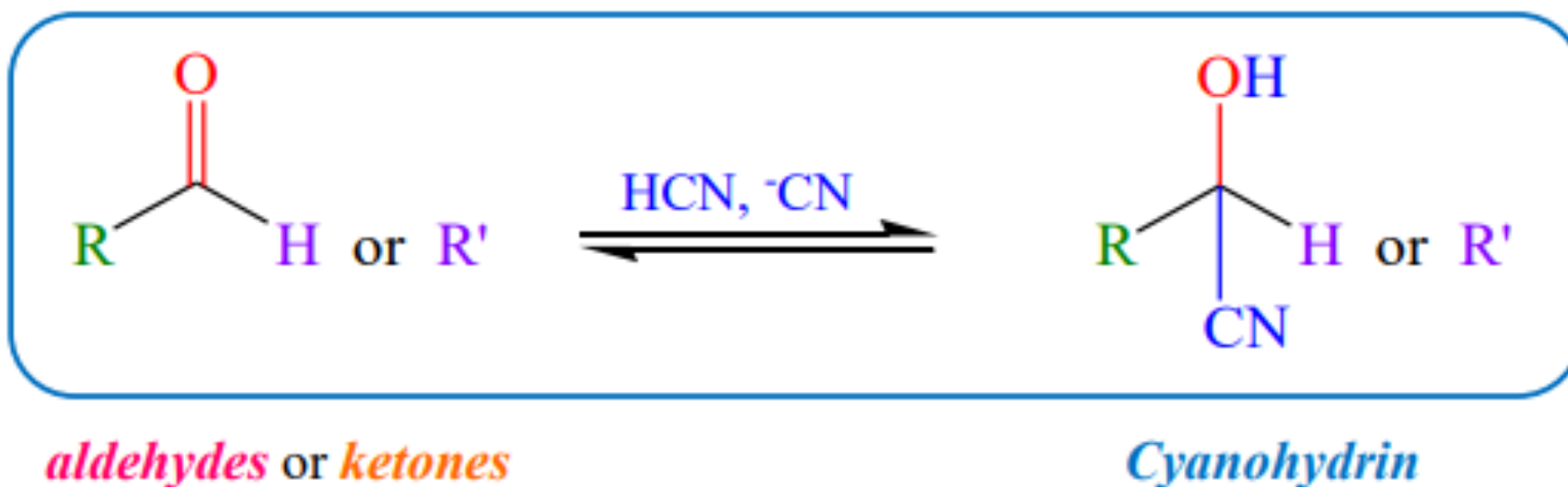
Compounds	Results	Why ??
HCHO	-ve, No yellow ppt	Has no CH_3CO
CH_3CHO	✓ +ve, gives yellow ppt	Has CH_3CO
CH_3COCH_3	✓ +ve, gives yellow ppt	Has CH_3CO
	-ve, No yellow ppt	Has no CH_3CO

Aldehydes and Ketones

5. Addition of Hydrogen cyanide: Formation of cyanohydrin.

✓ The nucleophilic addition of hydrogen cyanide (HCN) to aldehydes or ketones affords Cyanohydrin.

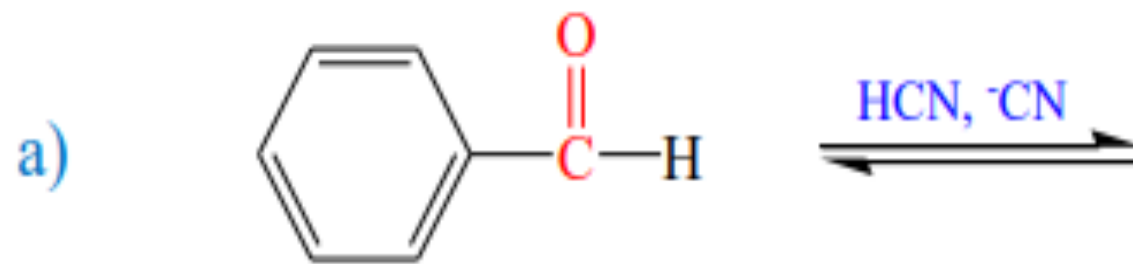
General equation



(**Cyanohydrin:** A molecule containing an **-OH** group and a **-CN** group bonded to the same carbon.

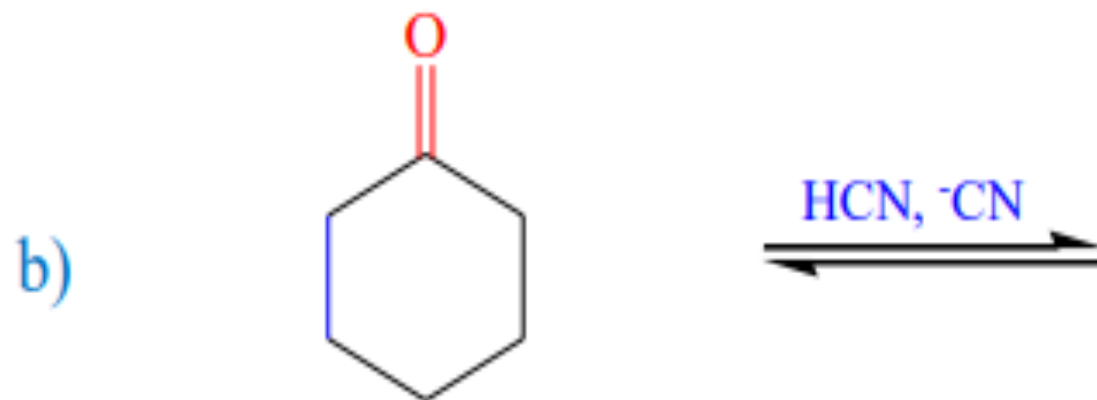
Aldehydes and Ketones

Examples:

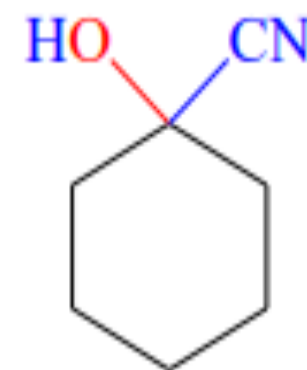


Benzaldehyde

Benzaldehyde cyanohydrin



Cyclohexanone

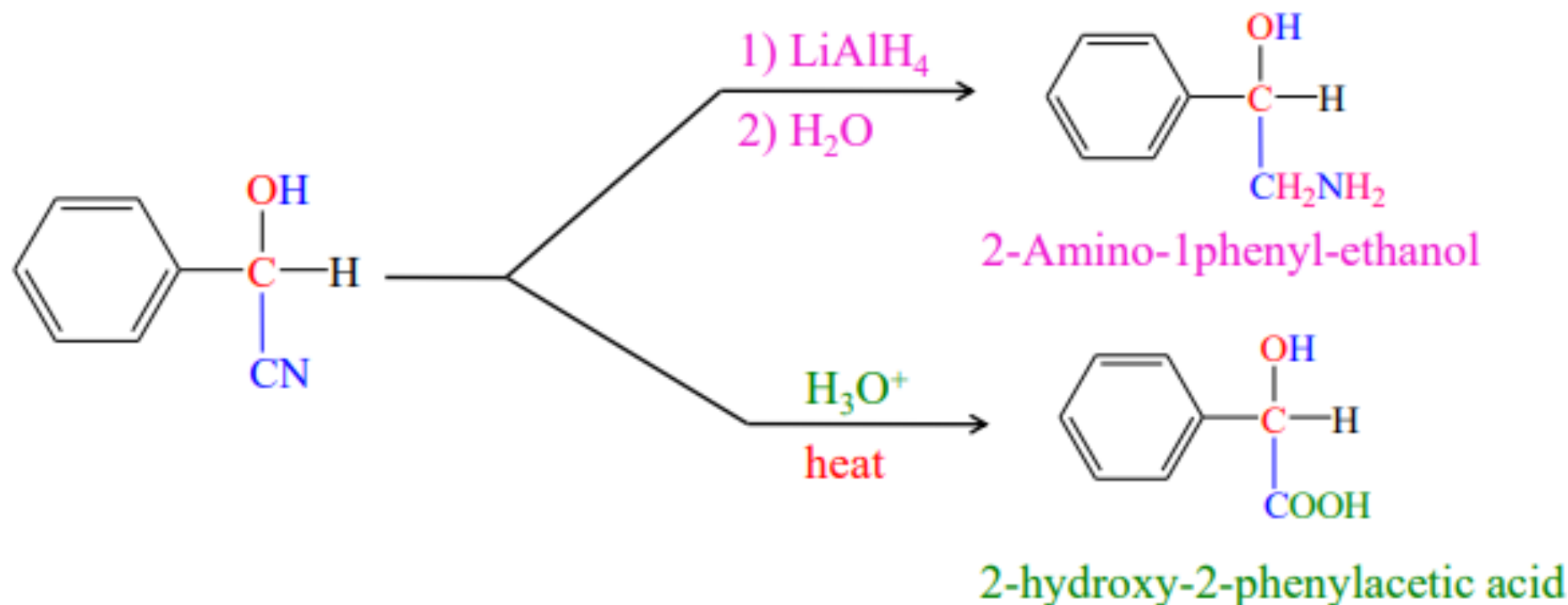


Cyclohexanone cyanohydrin

Aldehydes and Ketones

✓ Cyanohydrins are very useful because the CN group can be converted to other functional groups.

✓ For example: reduction with LiAlH_4 followed by water reduces the CN group to a primary amine. Thus an aminoalcohol product is formed.



✓ Also, hydrolysis of the CN group with acidic water gives a hydroxy carboxylic acid product. This affords us with an important method of synthesizing α -hydroxy-carboxylic acids.

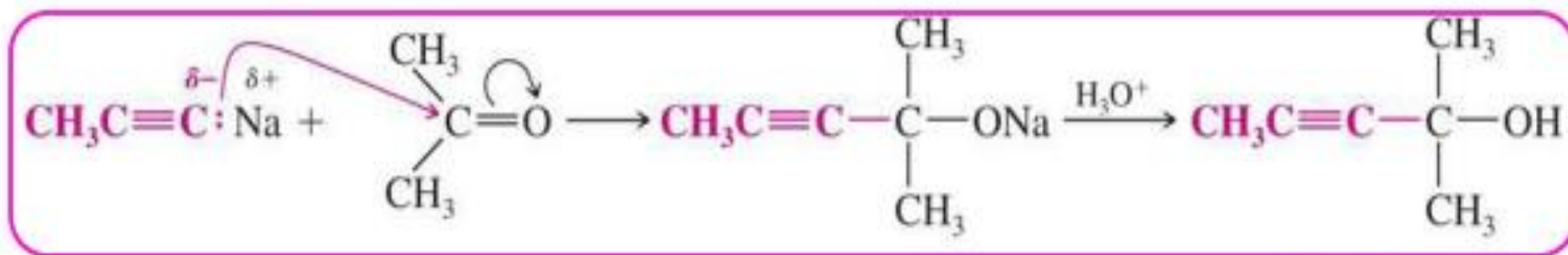
Aldehydes and Ketones

6- Nucleophilic addition of Acetylide ions:

✓ **Acetylide ions** are another example of **organometallic reagents**; it can be thought of as “**organo sodium reagents**”. They are good **nucleophiles**.

✓ **Acetylide ions** can also be used to attack **carbonyl group**, The net effect of the reaction of **organometallic reagents** with an **aldehyde** or **ketone** is the **addition** of the components **R** and **H** across the **C=O** double bond.

General equation



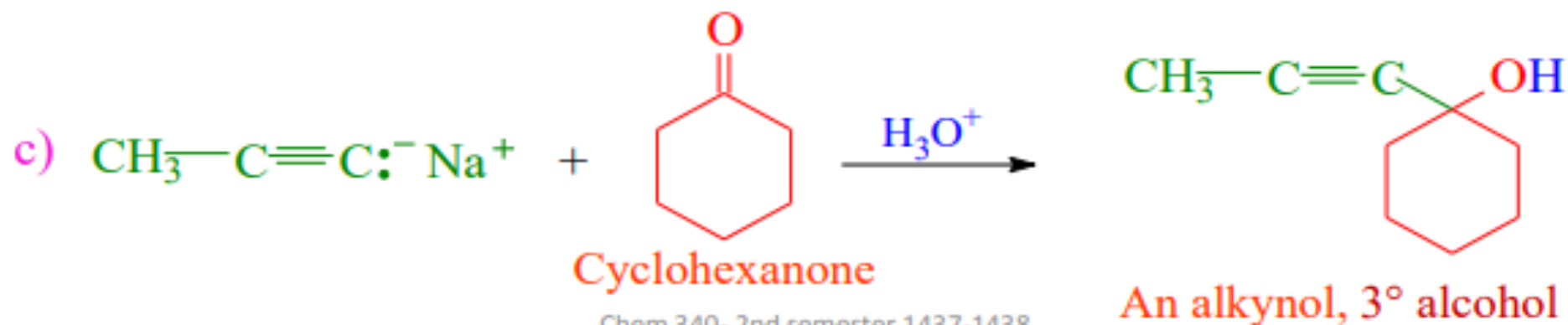
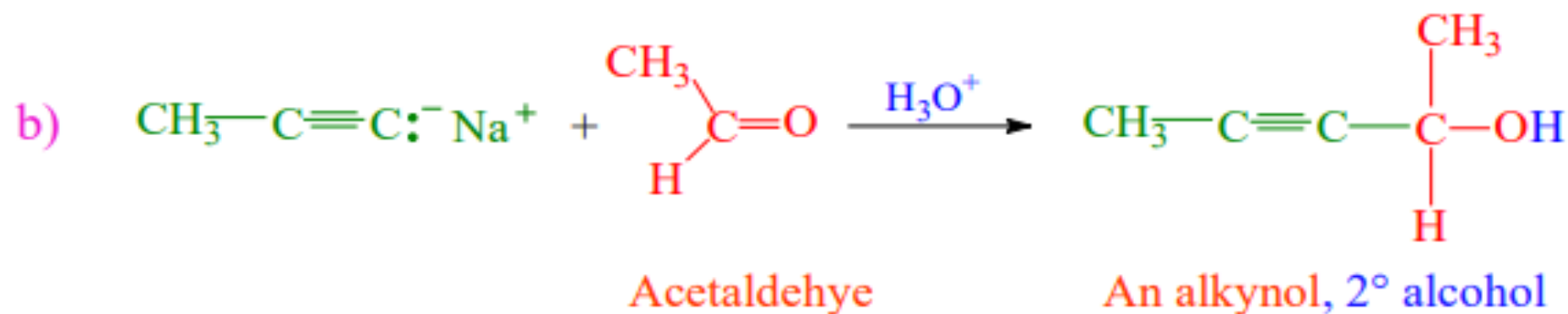
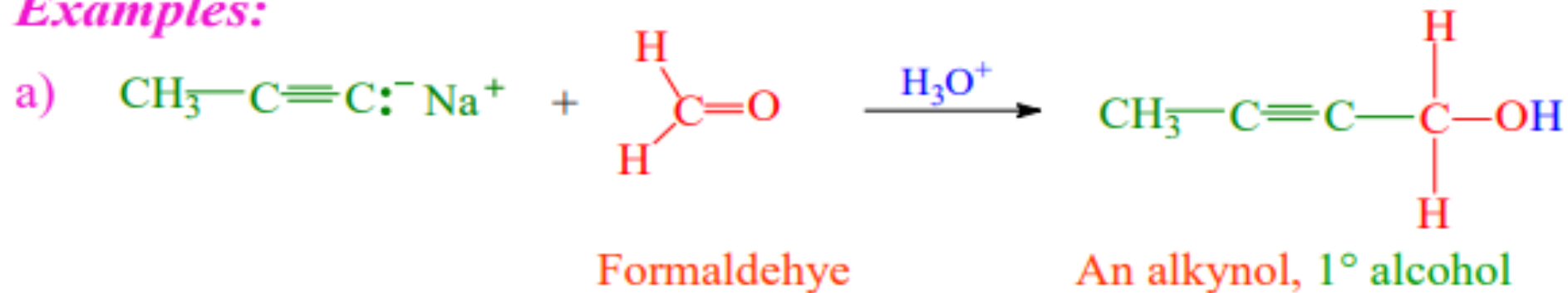
✓ The addition of **acetylides ions** to **aldehydes** and **ketones** yields **An alkynol** **an alkynol**.



(*An alkynol: is an alcohol on carbon adjacent to triple bond.*)

Aldehydes and Ketones

Examples:



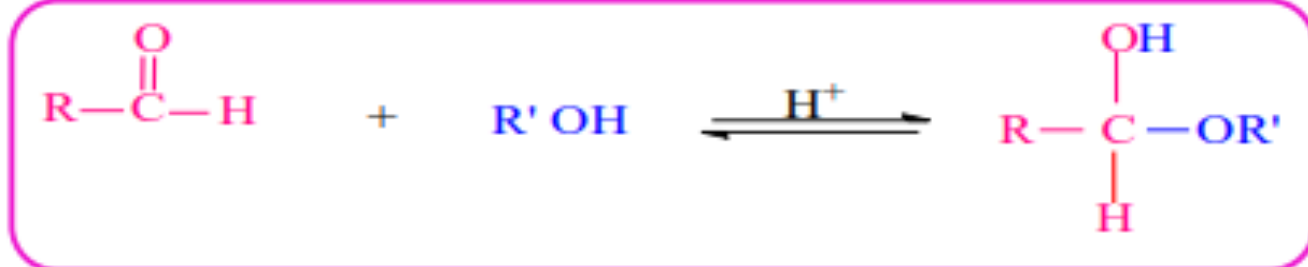
Aldehydes and Ketones

7- Nucleophilic Addition of Alcohols:

A.1 Hemiacetals Formation of Hemiacetals and Acetals

The addition of one mole of an alcohol to the carbonyl group of an aldehyde yields a hemiacetal. (*hemi*, Greek, half).

General equation



An Aldehyde

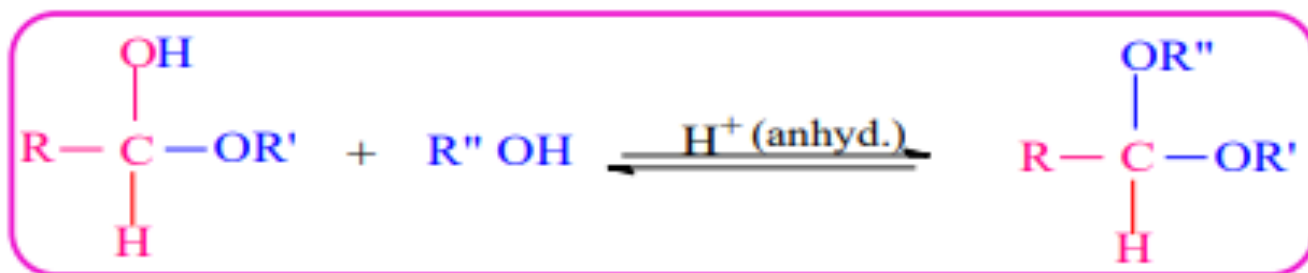
An alcohol

A hemiacetal

B.1 Acetals

When hemiacetals are treated with an additional mole of an alcohol in the presence of anhydrous acid, they are converted to acetals.

General equation



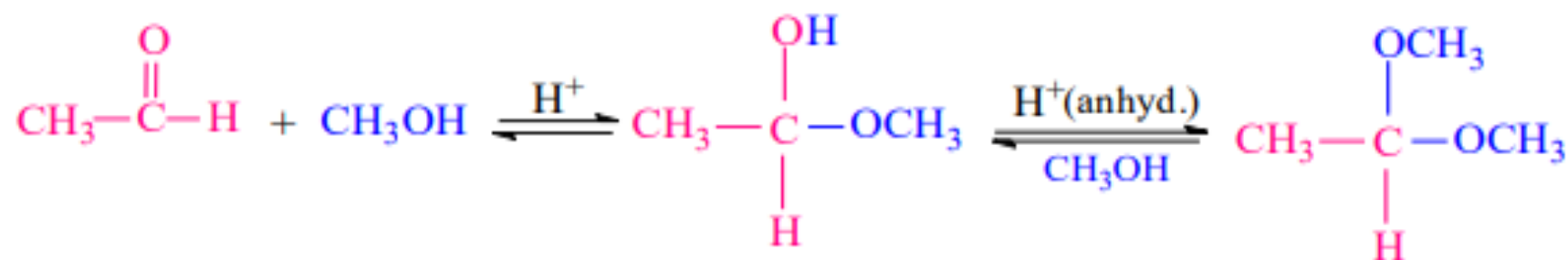
A hemiacetal

An alcohol

Acetals

Aldehydes and Ketones

Example



Ethanal

Methanol

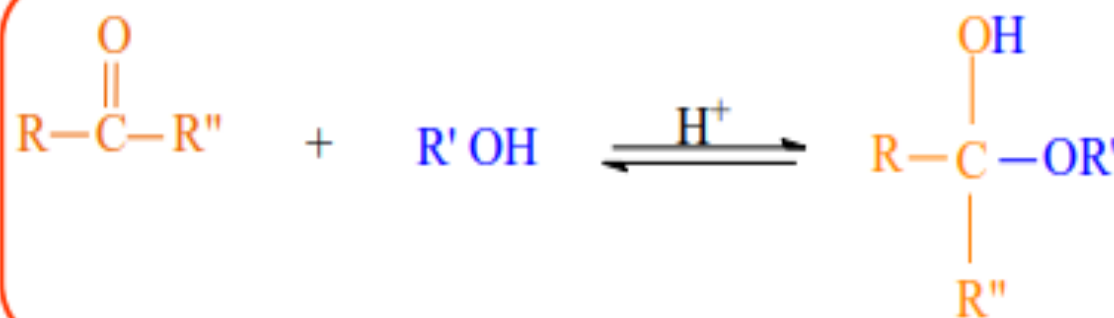
1-Methoxyethanol
(A hemiacetal)

1,1-Dimethoxyethanol
(An acetal)

A.2 Hemiketals

The addition of one mole of an alcohol to the carbonyl group of a ketone yields a hemiketal.

General equation



A Ketone

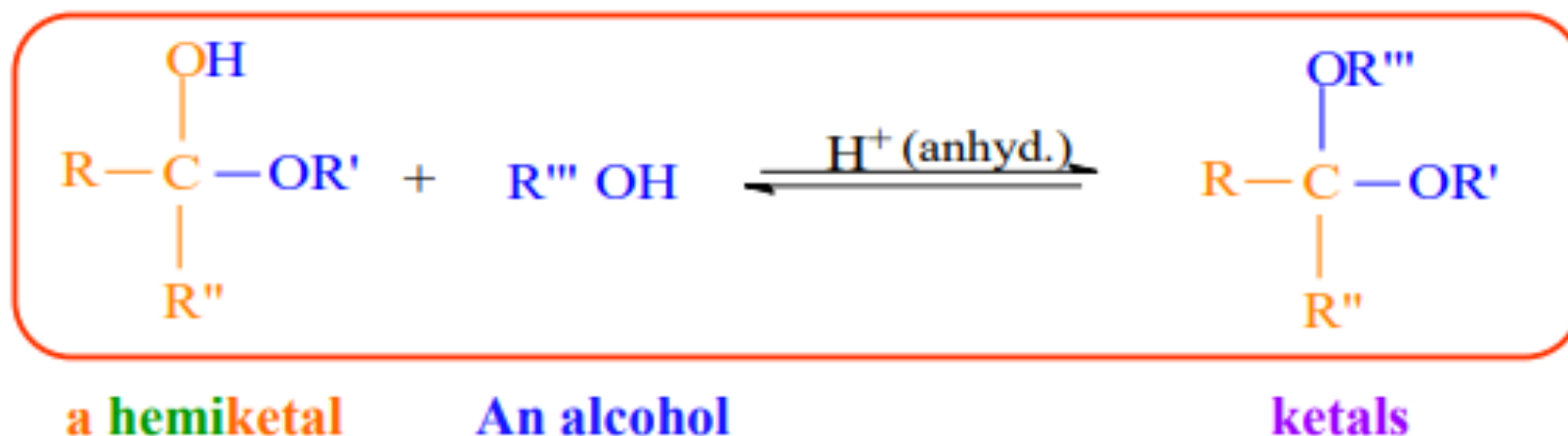
An alcohol

A hemiketal

Aldehydes and Ketones

B.2 Ketals

The reaction of hemiketal with alcohols to form ketals is *seldom* works.



The Conclusion

- ✓ The *hemiacetal* and the *hemi ketal* are compounds that have an alkoxy group (OR) & hydroxy group (OH) that are attached to the same carbone.
- ✓ The *acetals* & the *ketals* are compounds that have two alkoxy groups (OR) on the same carbon.

Aldehydes and Ketones

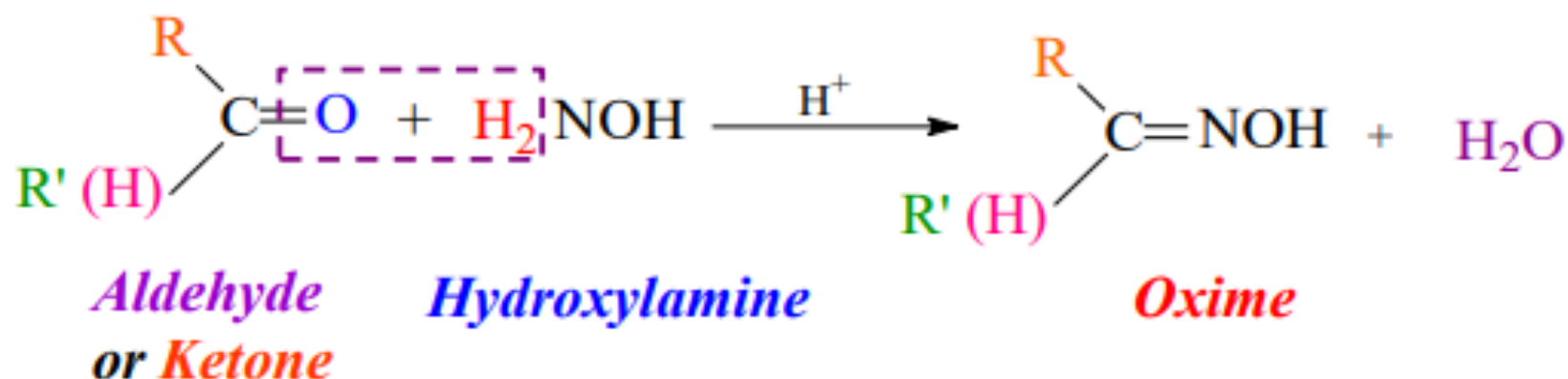
8- Addition of Ammonia and Ammonia Derivatives

- ✓ Nitrogen nucleophiles such as ammonia and its derivatives $\text{H}_2\text{N} - \text{Z}$ add to carbonyl group of **aldehydes** and **ketones**.
- ✓ The reaction is **reversible** and **catalysed** by **acid**.

✓ The net result is replacement of the $>\text{C} = \text{O}$ group with $>\text{C} = \text{N} - \text{Z}$ group

a) The Reaction with Hydroxylamine

Aldehydes and **ketones** react with **hydroxylamine** to form **oximes**.

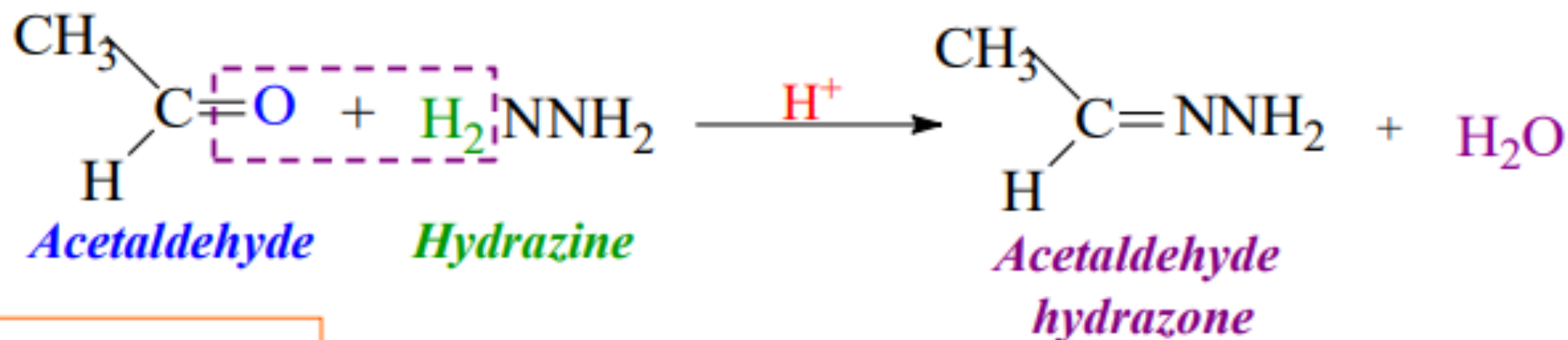


Aldehydes and Ketones

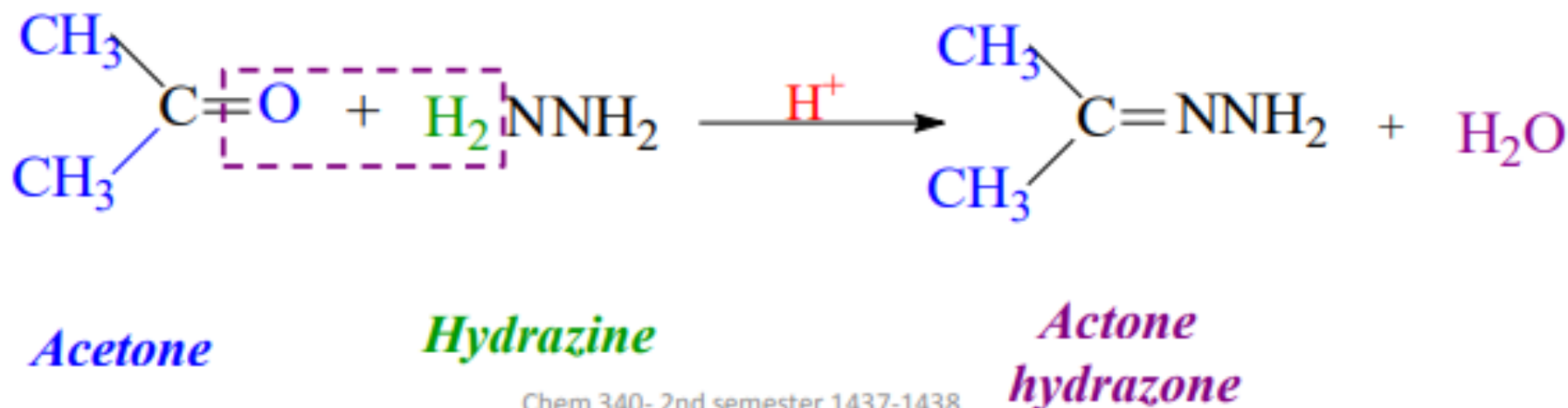
b) The Reaction with Hydrazine

Aldehydes and ketones react with hydrazine to form hydrazones.

With aldehydes



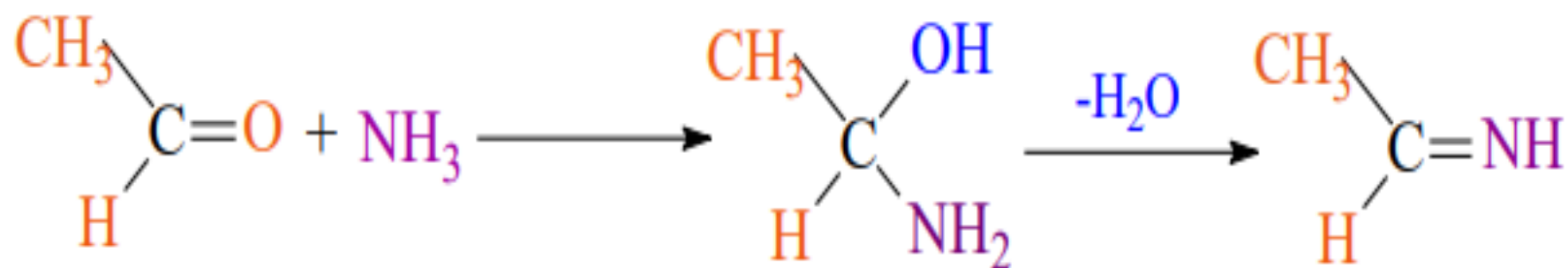
With ketones



Aldehydes and Ketones

c) The Reaction with ammonia NH_3

Like ammonia derivatives ammonia also reacts with **aldehydes** (except formaldehyde) and **ketones** to form the products called **imines**.



Acetaldehyde Ammonia

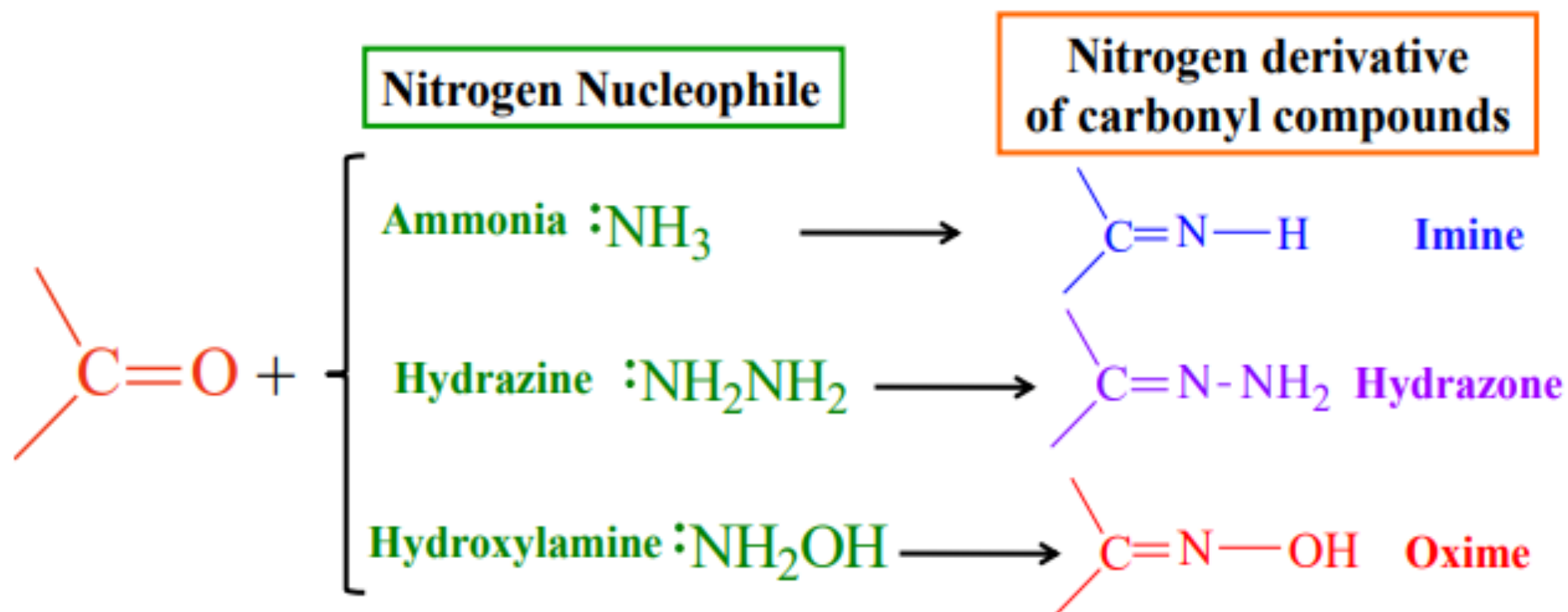
*Acetaldehyde
ammonia*

Acetaldimine

Aldehydes and Ketones

Summary

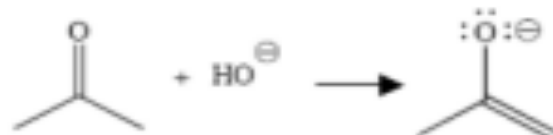
Structure and names of nitrogen nucleophiles that react with carbonyl compounds:



Aldehydes and Ketones

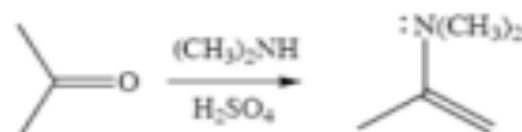
Structure, Reactivity, General formation

Enolate



Enolate = negative charge on oxygen with adjacent C-C double bond

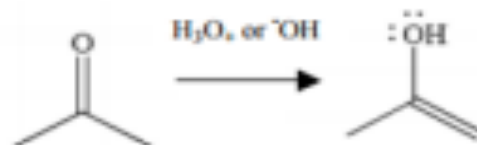
Enamine



Enamine = NR_2 group adjacent C-C double bond

Reacts in similar way as enolates

Enol

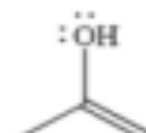
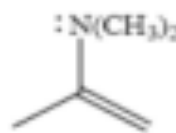
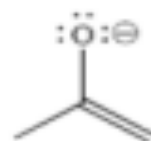


Enol = hydroxyl group with adjacent C-C double bond

Alkene + alcohol = enol

Order of Decreasing Nucleophilic reactivity

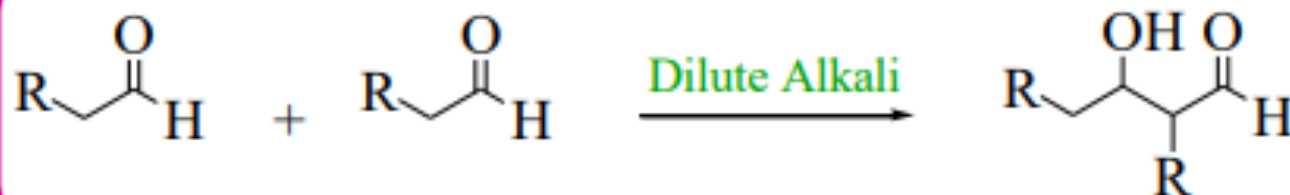
ENOLATE > ENAMINE > ENOL



*electron-rich pi bond is a source of nucleophilic character in all three

Aldehydes and Ketones

9- Aldol condensation



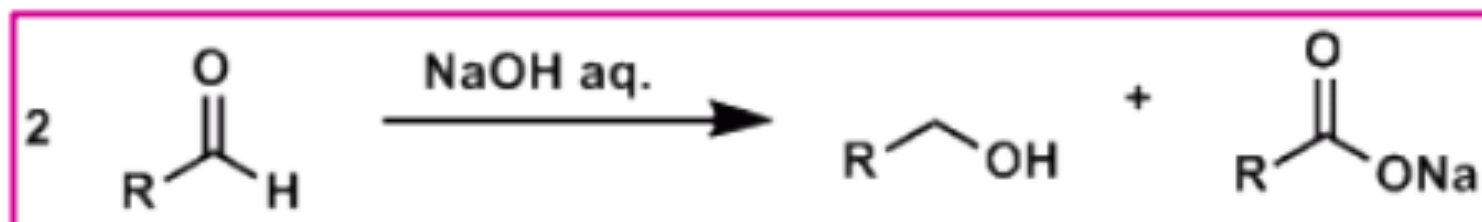
- **Aldol** means **aldehyde** and **alcohol** groups on the same molecule.
- May occur between **two aldehydes** (aldols) or **two ketones** (ketols) in the presence of **catalytic base**.
- Reaction **ONLY** possible between **two components** having **α -hydrogen**.
- The reactions are reversible
 - With Aldehydes, the equilibrium favors product
 - With ketones, the equilibrium favors the starting materials.

Aldehydes and Ketones

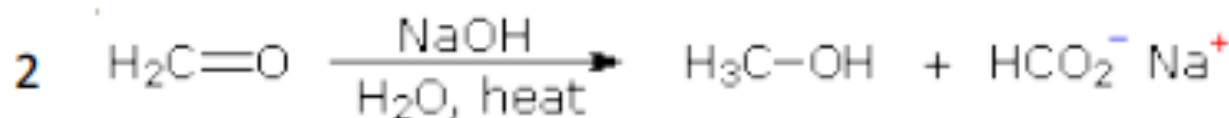
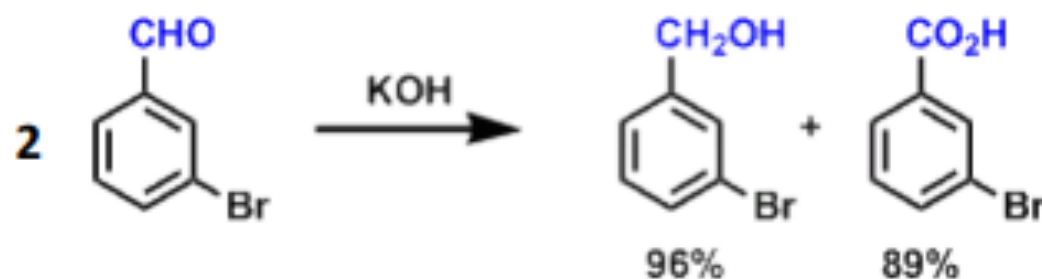
10- Cannizzaro Reaction

Upon treatment with strong bases (e.g. in aqueous NaOH) and heating, non-enolizable aldehydes undergo **redox disproportionation** to give corresponding alcohols and carboxylic acids in 1:1 ratio.

General equation

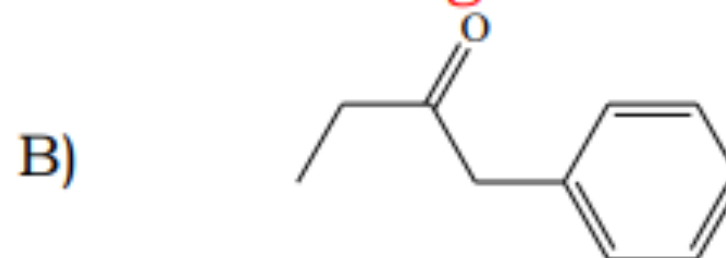
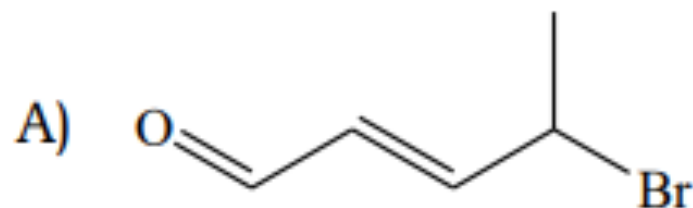


Examples



Aldehydes and Ketones

Q.2. Give the IUPAC name for the following.



Q.3 Arrange these compounds in order of **increasing** Boiling point.

Acetone	Propan-1-ol	Propanal	<i>n</i> -Butane	Methoxyethane
(i)	(ii)	(iii)	(iv)	(v)

Aldehydes and Ketones

Example (1):

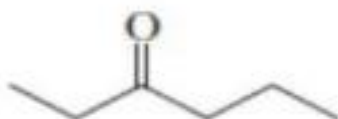
Write structural formulas for all ketones with the molecular formula $C_6H_{12}O$ and give each its IUPAC name.

Solution

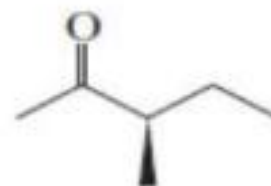
Following are line-angle formulas and IUPAC names for the six ketones with this molecular formula.



2-Hexanone



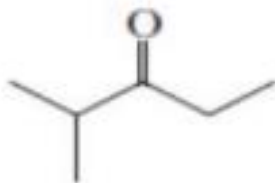
3-Hexanone



3-Methyl-2-pentanone



4-Methyl-2-pentanone



2-Methyl-3-pentanone



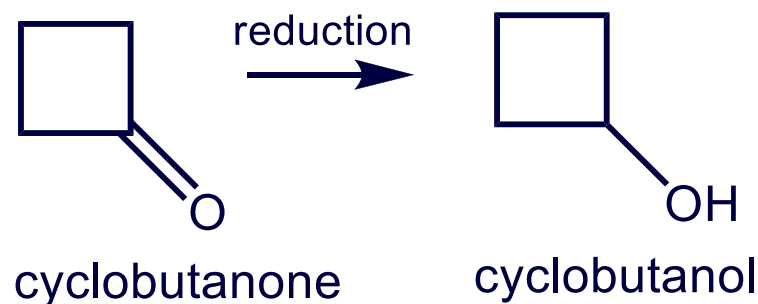
3,3-Dimethyl-2-butanone

XXXX

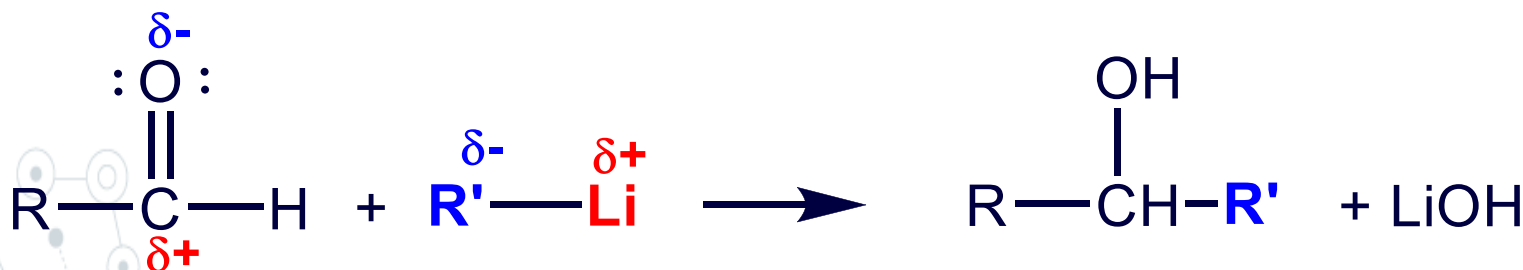
Aldehydes and Ketones

□ Reactions of Aldehydes and Ketones

- **Reduction** to alcohols is an example of an *addition* reaction:



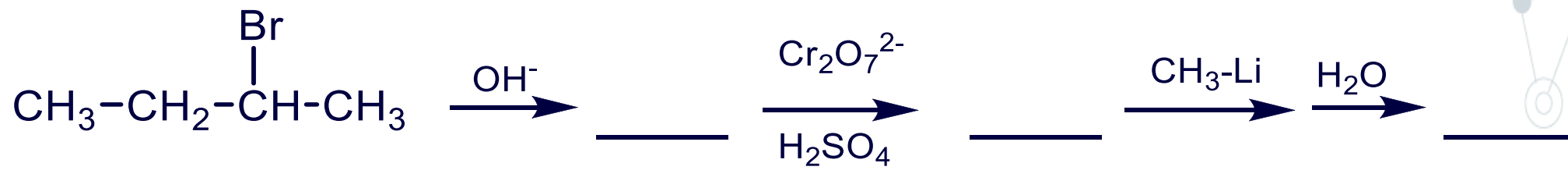
- **Organometallic** compounds, which have a metal atom covalently bonded to C, add to the electron-poor carbonyl C:



Aldehydes and Ketones

Sample Problem: Predicting the Steps in a Reaction Sequence?

PROBLEM: Fill in the blanks in the following reaction sequence:

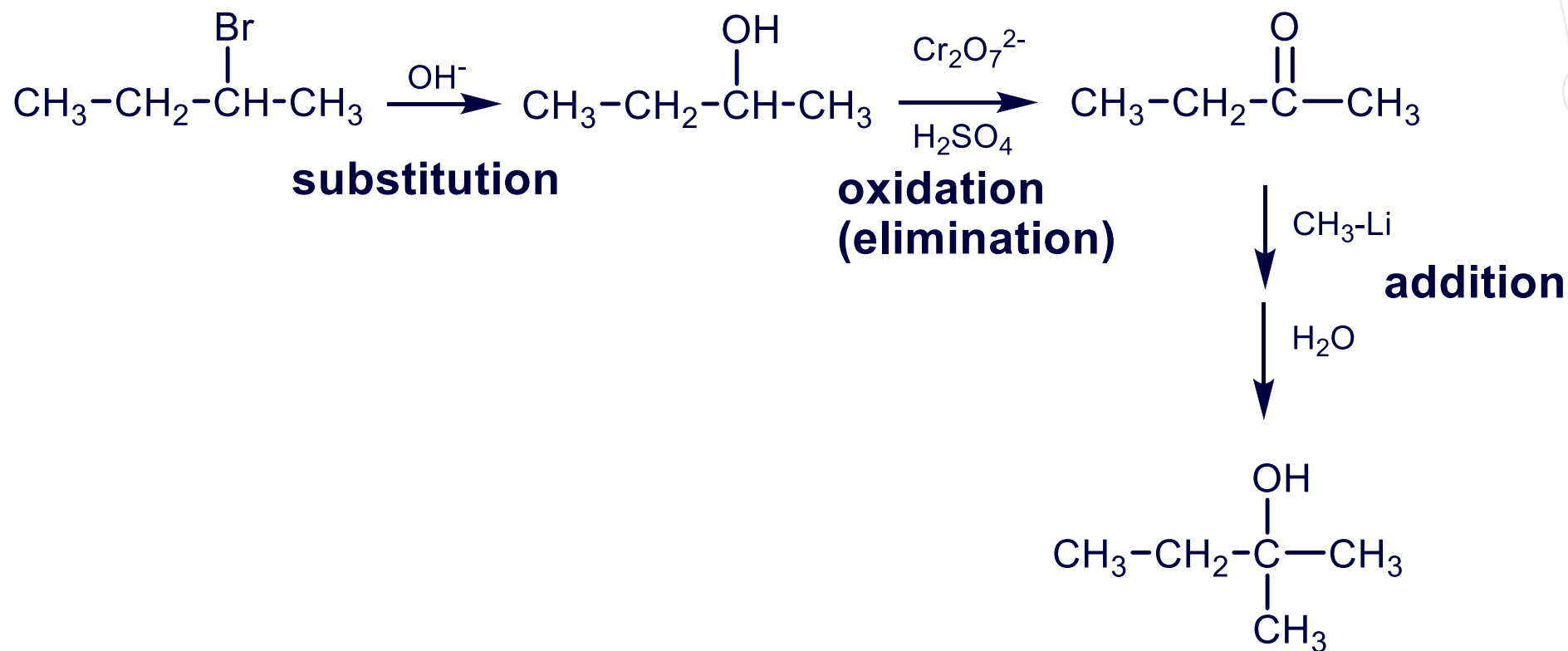


PLAN: For each step we examine the functional group of the reactant and the reagent above the yield arrow to decide on the most likely product.

SOLUTION: The first step involves an alkyl halide reacting with OH^- , so this is probably a substitution reaction, which yields an alcohol. In the next step the alcohol is oxidized to a ketone and finally the organometallic reagent adds to the ketone to give an alcohol with one more C in its skeleton:

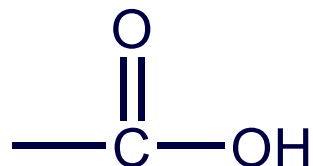
Aldehydes and Ketones

SOLUTION:

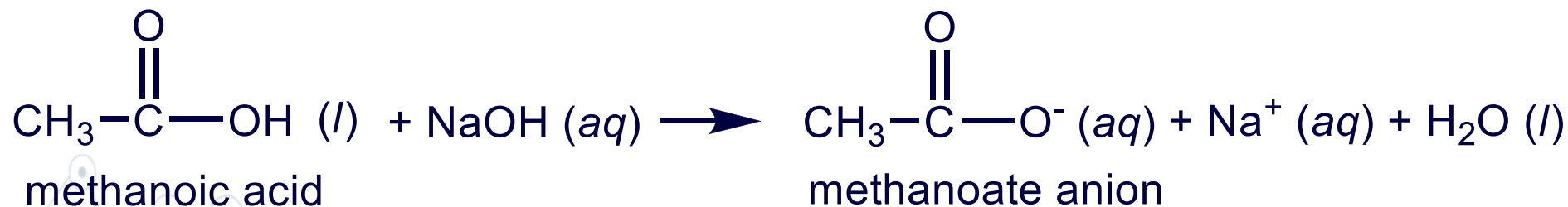


Carboxylic Acids

- Carboxylic acids contain the functional group **-COOH**, or



- Carboxylic acids are named by replacing the *-e* of the alkane with the **suffix *-oic acid***.
- Carboxylic acids are **weak acids** in water, and react with strong bases:



Carboxylic Acids

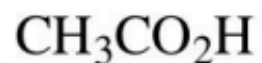
Common Nomenclature

Prefix

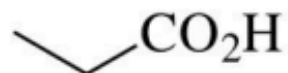
form



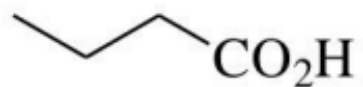
acet



propion



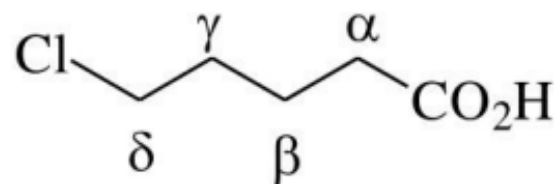
butyr



valer



prefix + ic + _acid

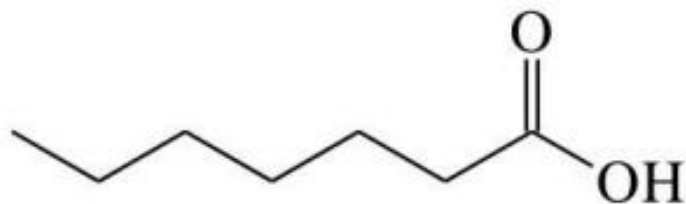


δ -chlorovaleric acid

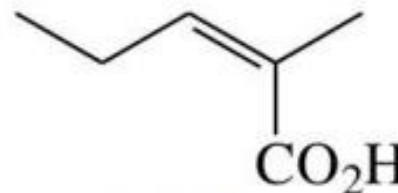
Carboxylic Acids

I.U.P.A.C. Nomenclature

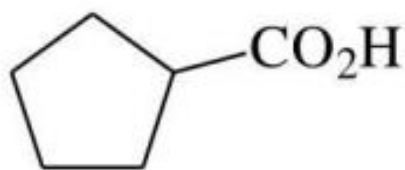
drop **e** from alkane and add "oic acid"



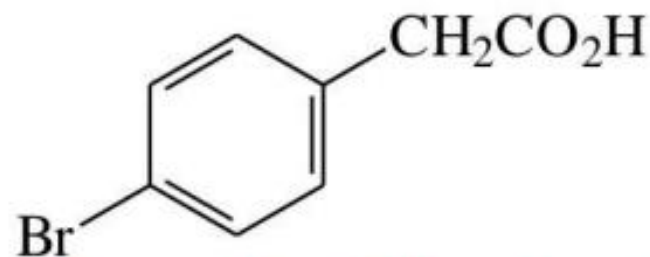
heptanoic acid



(Z) 2-methyl-2-pentenoic acid



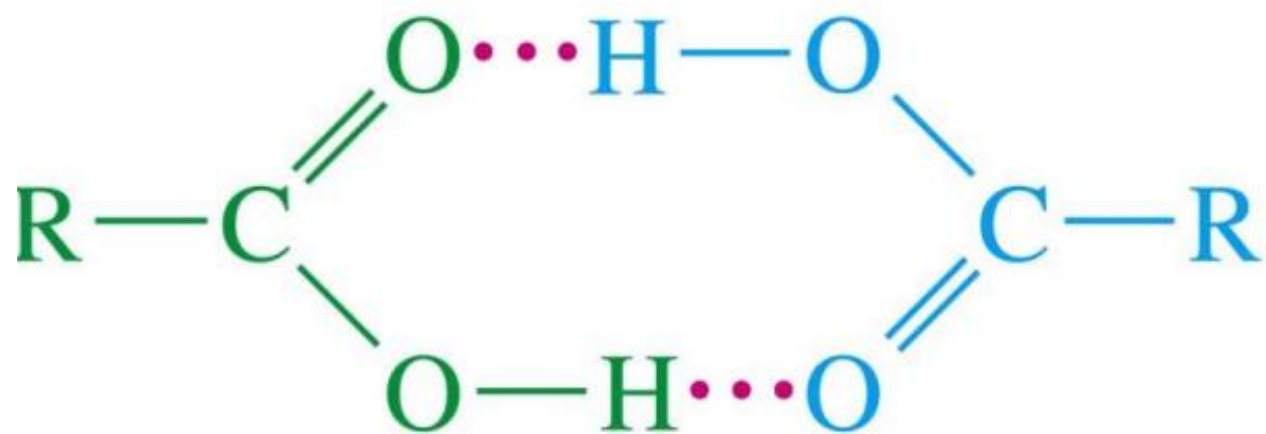
cyclopentanecarboxylic acid



p-bromophenylethanoic acid
p-bromophenylacetic acid

Carboxylic Acids

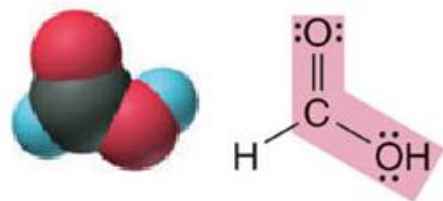
Unusually High Melting and Boiling Points



hydrogen-bonded acid dimer

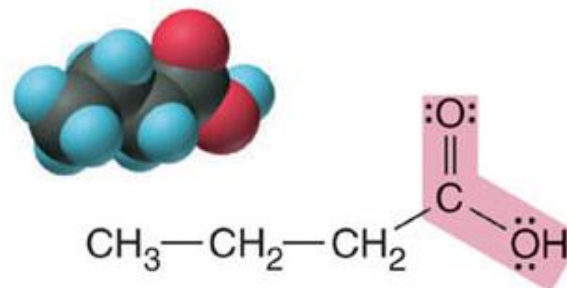
Carboxylic Acids

➤ Some molecules with the carboxylic acid functional group.



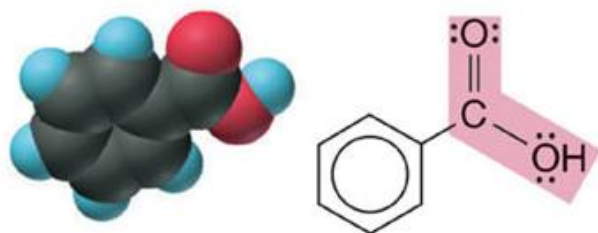
Methanoic acid (formic acid)

An irritating component of ant and bee stings



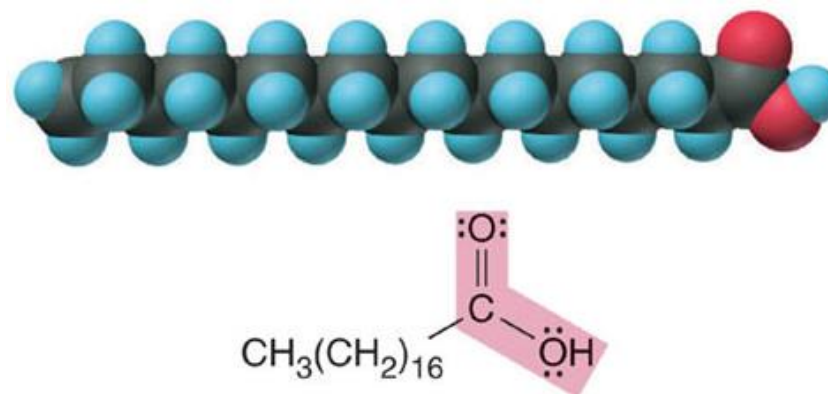
Butanoic acid (butyric acid)

Odor of rancid butter; suspected component of monkey sex attractant



Benzoic acid

Calorimetric standard; used in preserving food, dyeing fabric, curing tobacco



Octadecanoic acid (stearic acid)

Found in animal fats; used in making candles and soaps

Carboxylic Acids

➤ RCOOH Preparation Reactions

- ❖ **Oxidation of Primary Alcohols**
- ❖ **Oxidation of Aldehydes**
- ❖ **Oxidation of Substituted Aromatics**
- ❖ **Carbonation of Grignard reagents**
- ❖ **Hydrolysis of Acid derivatives and Nitriles**
- ❖ **Haloform reaction**
- ❖ **Periodic acid Cleavage of Vicinal Dials/Diketones**
- ❖ **Oxidative Cleavage of Alkenes/Alkynes**

Carboxylic Acids

➤ RCOOH Preparation Reactions

- Oxidation of 1° alcohols and aldehydes with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$
- KMnO_4 oxidation of alkylbenzenes
- Grignard reaction with CO_2 (Carboxylation)
- Hydrolysis of a carboxylic derivative:
e.g. acid chloride, acid anhydride, ester,
amide, nitrile

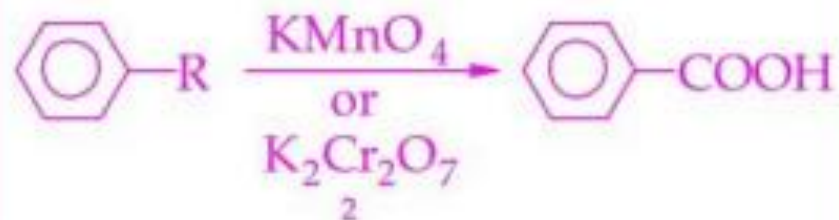
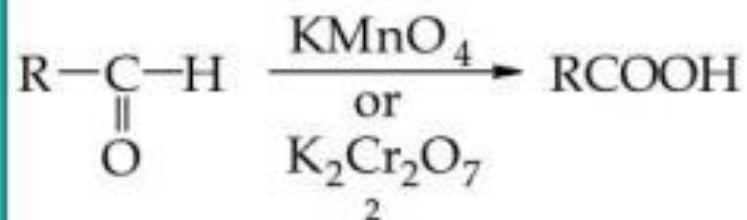
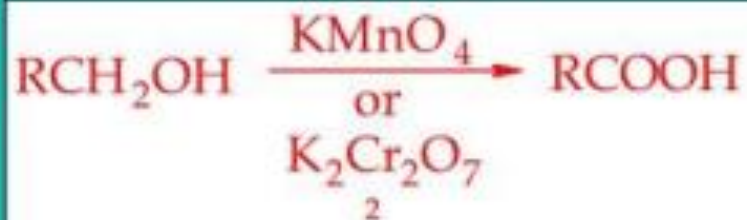
Carboxylic Acids

➤ Carboxylic Acids via Oxidation

◆ From Primary Alcohols

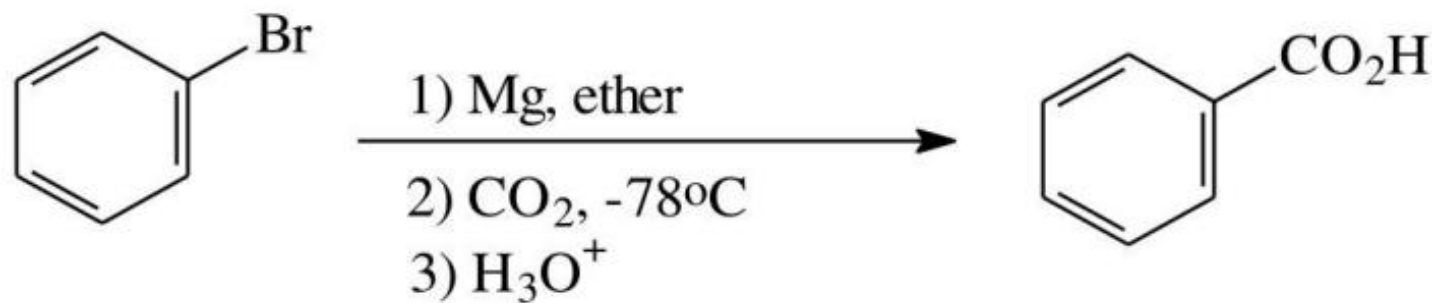
◆ From Aldehydes

◆ From Substituted Aromatics



Carboxylic Acids

➤ Grindar Reaction with CO_2



Carboxylic Acids

➤ Typical RCOOH Reactions

- ✠ **Conversion to carboxylate salts**
- ✠ **Conversion to acid halides**
- ✠ **Conversion to esters**
- ✠ **Conversion to amides**
- ✠ **Conversion to anhydrides**
- ✠ **Reduction to alcohols**
- ✠ **Decarboxylation**



Carboxylic Acids

➤ Carboxylates from Carboxylic Acids

❖ Reaction with Active Metals

❖ Reaction with Strong Base

❖ Reaction with Weak Base



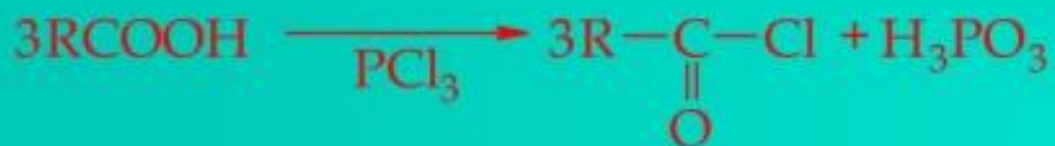
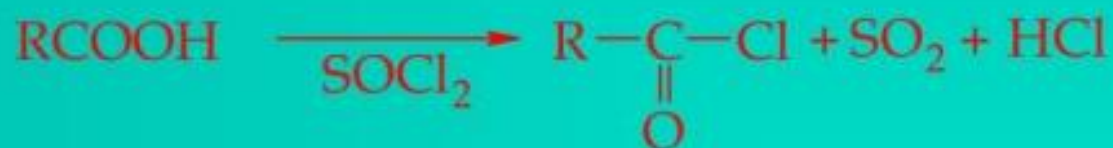
Carboxylic Acids

➤ Acid Chlorides from Carboxylic Acids

➤ Reaction with Thionyl Chloride

➤ Reaction with Phosphorus Trichloride

➤ Reaction with Phosphorus Pentachloride



Carboxylic Acids

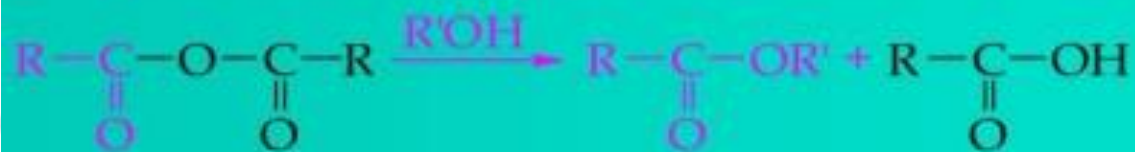
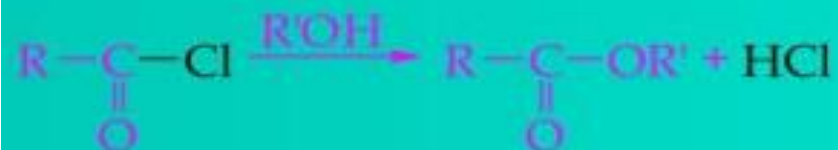
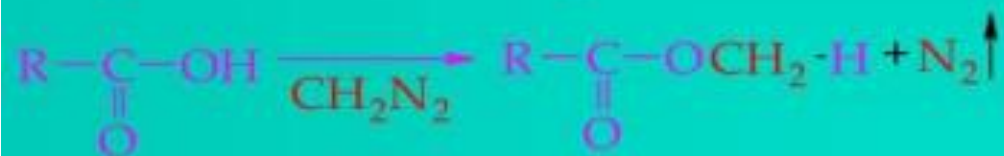
➤ Ester Formation

✧ From Carboxylic Acids

with ROH via mineral acid catalysis
via the use of diazomethane

✧ From Acid Chlorides

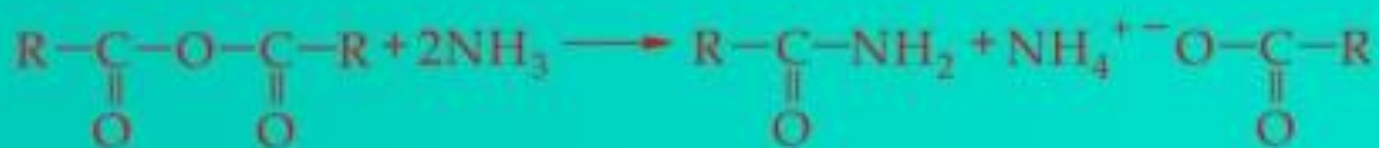
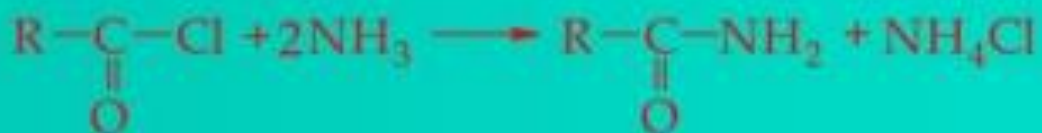
✧ From Acid Anhydrides



Carboxylic Acids

➤ Amide Formation

- ✧ **Direct Conversion of Acids to Amides**
- ✧ **From Acid Chlorides**
- ✧ **From Acid Anhydrides**
- ✧ **From Esters**

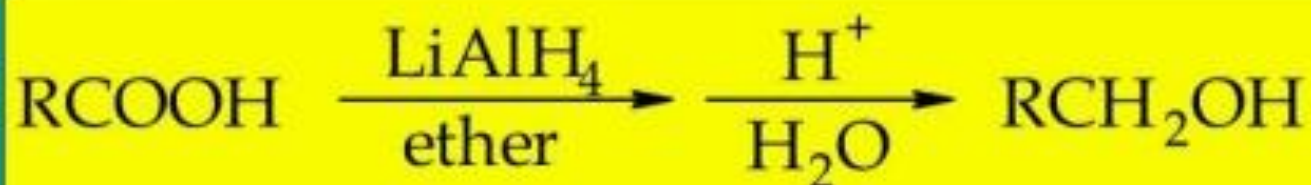


Carboxylic Acids

➤ Reduction of Carboxylic Acids

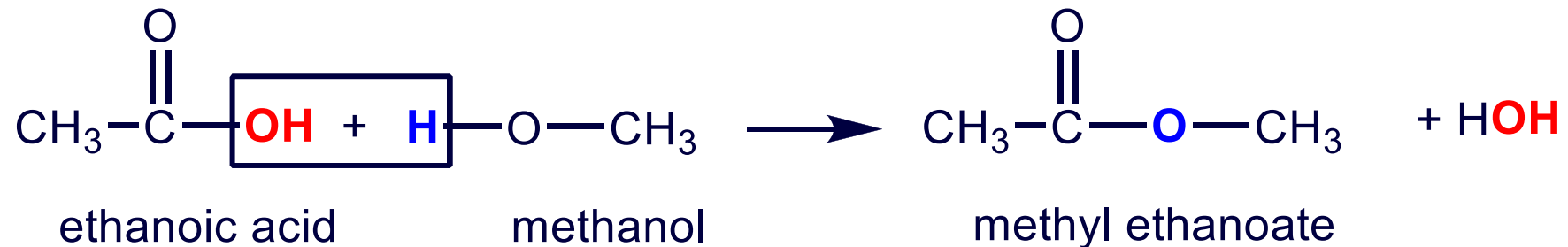
◆ **Lithium Aluminum Hydride reduction**

◆ **Diborane reduction**



Esters

- ❑ The ester group is formed by the reaction of an alcohol and a carboxylic acid.



Esterification is a dehydration-condensation reaction.

- ❑ Ester groups occur commonly in ***lipids***, which are formed by the esterification of fatty acids.

Esters

Naming Esters:

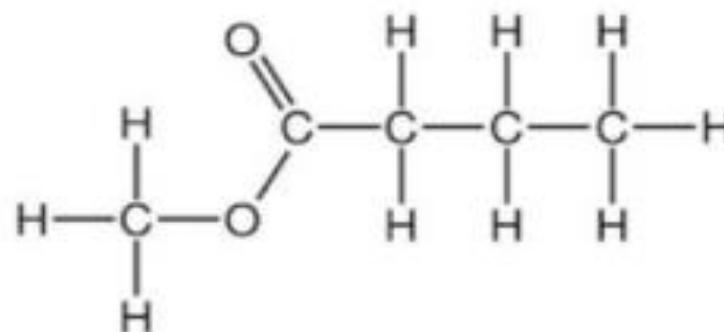
Name the alkane parent, drop the “e”, replace with “oate”
then name the branch that the is after the =O but you write it first.

Simple! Right?

Methyl butanoate



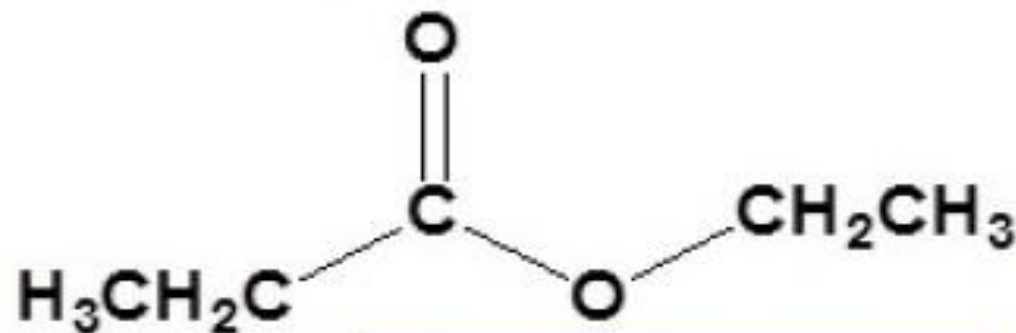
Methyl Butanoate



methyl butanoate

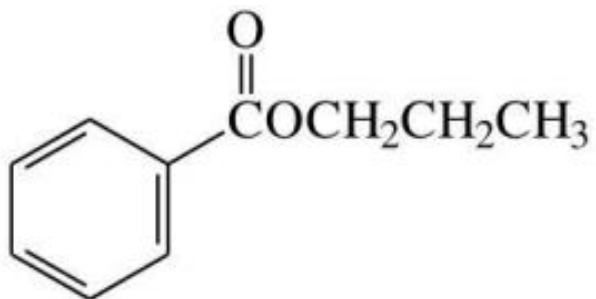


Ethyl Propanoate

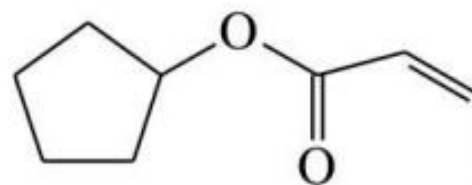


Ethyl propanoate

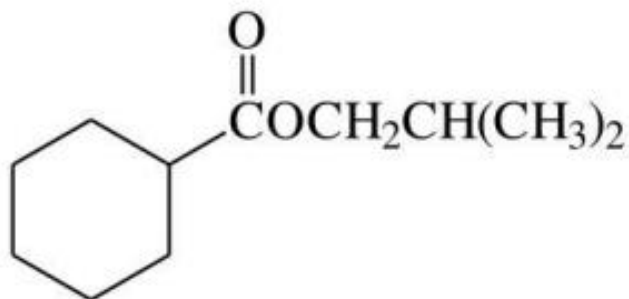
Esters



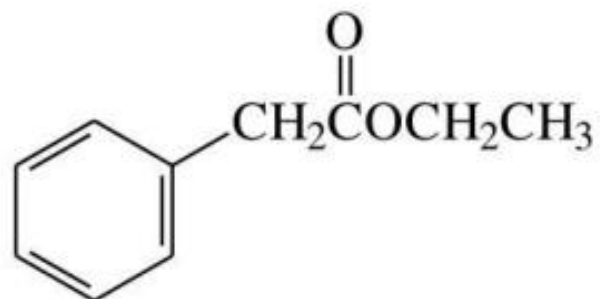
propyl benzoate



(Z) cyclopentyl 2-butenate



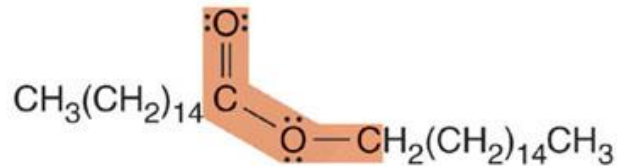
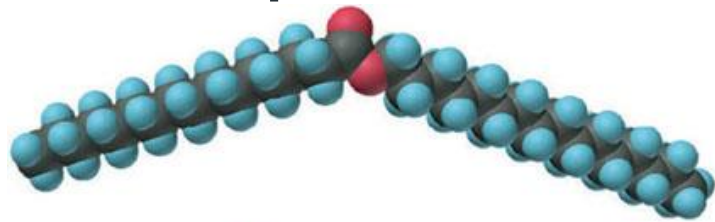
isobutyl cyclohexanecarboxylate



ethyl phenylacetate

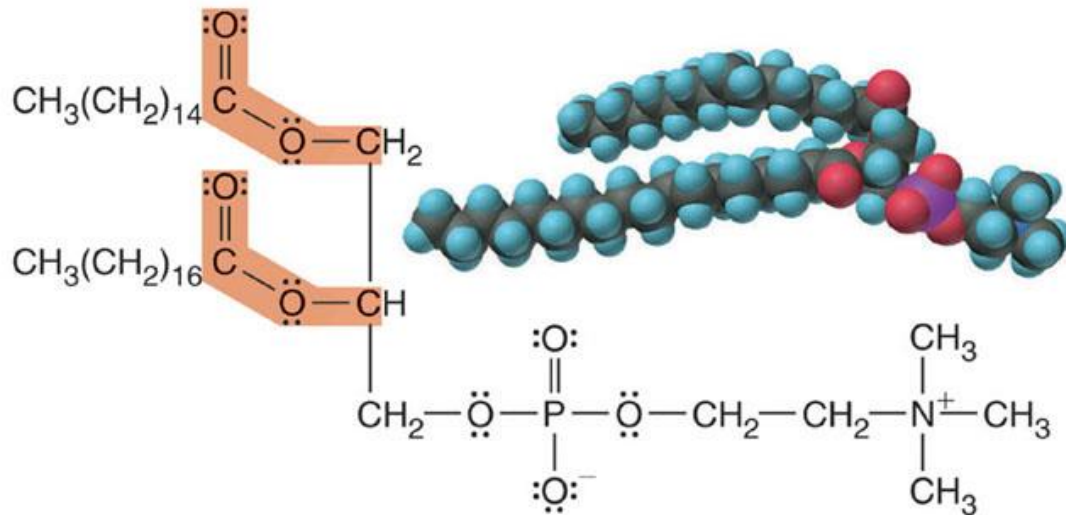
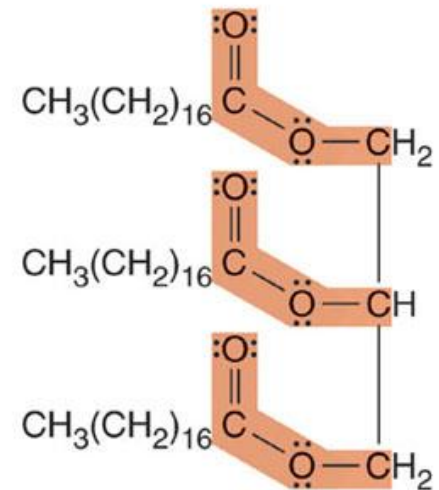
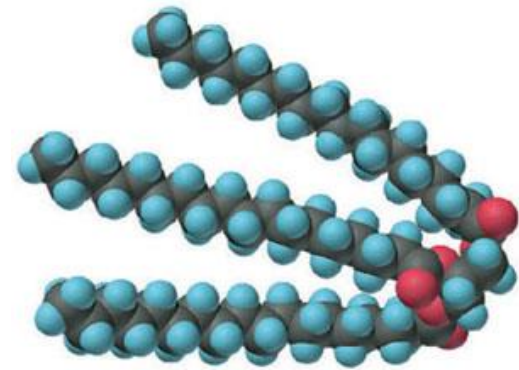
Esters

❖ Some lipid molecules with the ester functional



Cetyl palmitate

The most common lipid in whale blubber



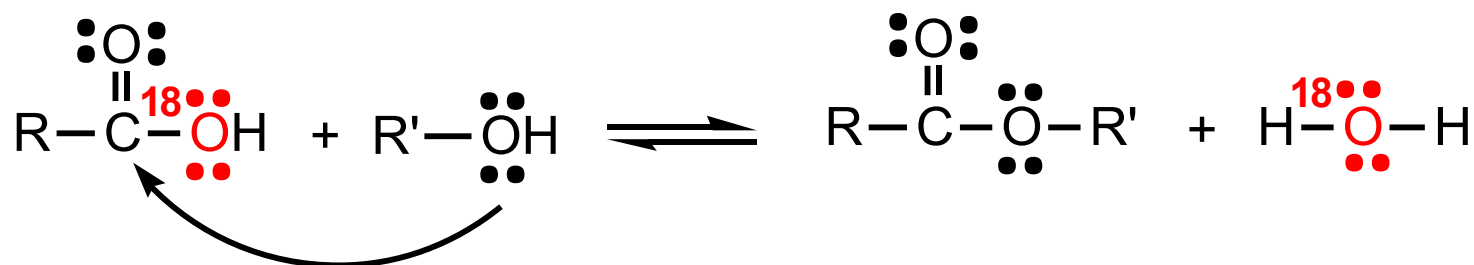
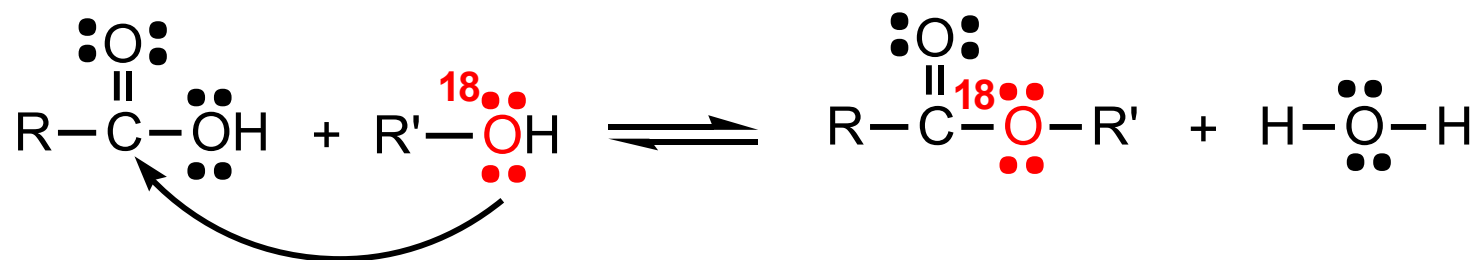
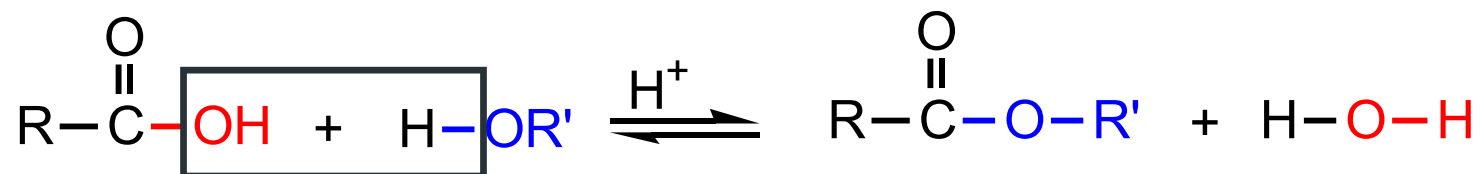
Lecithin Phospholipid found in all cell membranes

Tristearin Typical dietary fat used as an energy store in animals

Esters

❖ Which reactant contributes which group to the ester?

General esterification reaction

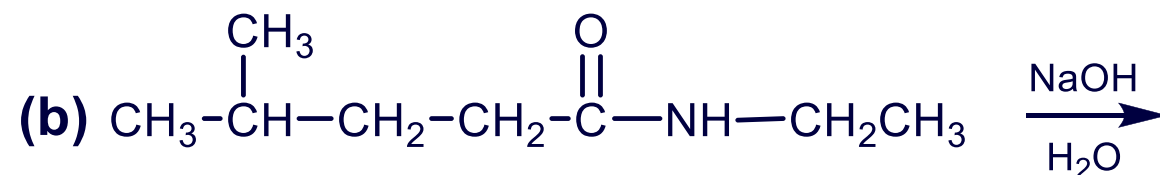
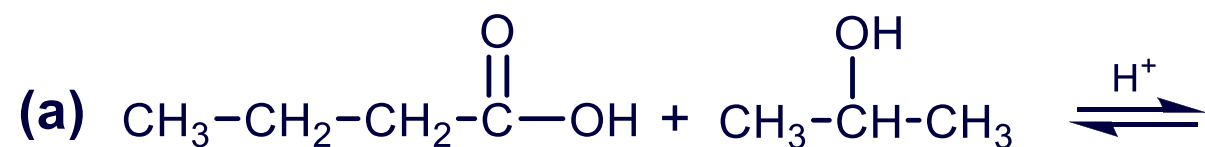


Esters

Sample Problem:

Predicting the Reactions of the Carboxylic Acid Family?

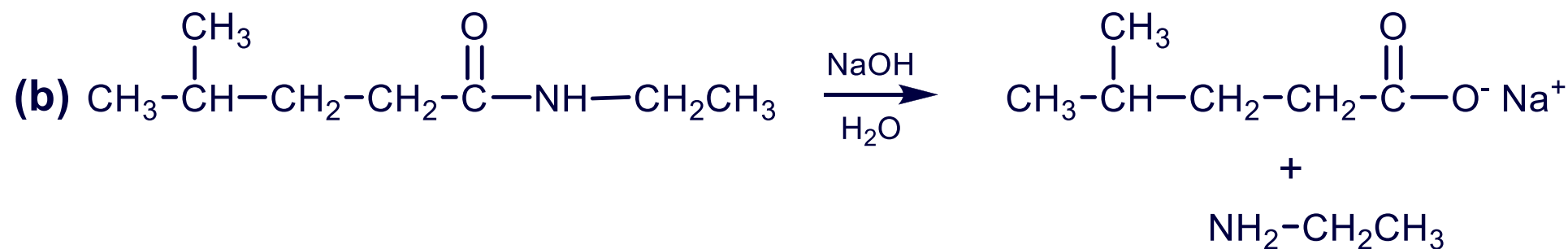
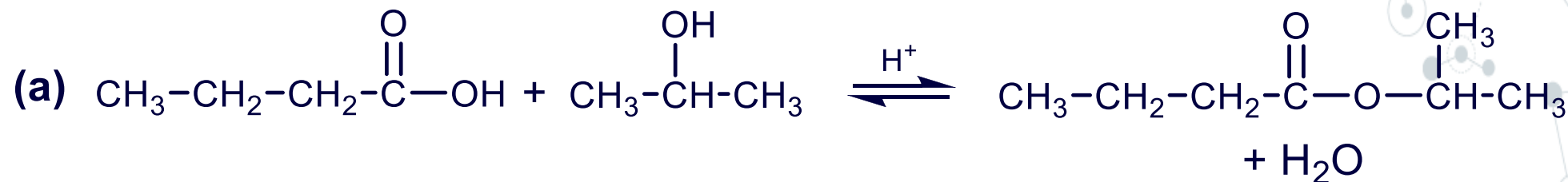
PROBLEM: Predict the product(s) of the following reactions:



PLAN: We identify the functional groups in the reactant(s) and see how they change. In (a), a carboxylic acid reacts with an alcohol, so the reaction must be a substitution to form an ester. In (b), an amide reacts with aqueous base, so hydrolysis occurs.

Esters

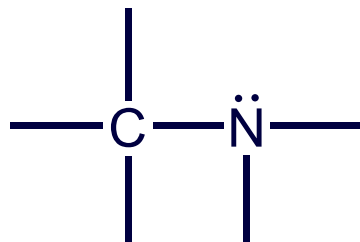
SOLUTION:



Amines



- The amine functional group contains a N atom.



- The systematic name for an amine is formed by dropping the final *-e* of the alkane and adding the **suffix *-amine***.
- Common names that use the name of the alkyl group followed by the suffix *-amine* are also widely used.



ethanamine OR
ethylamine



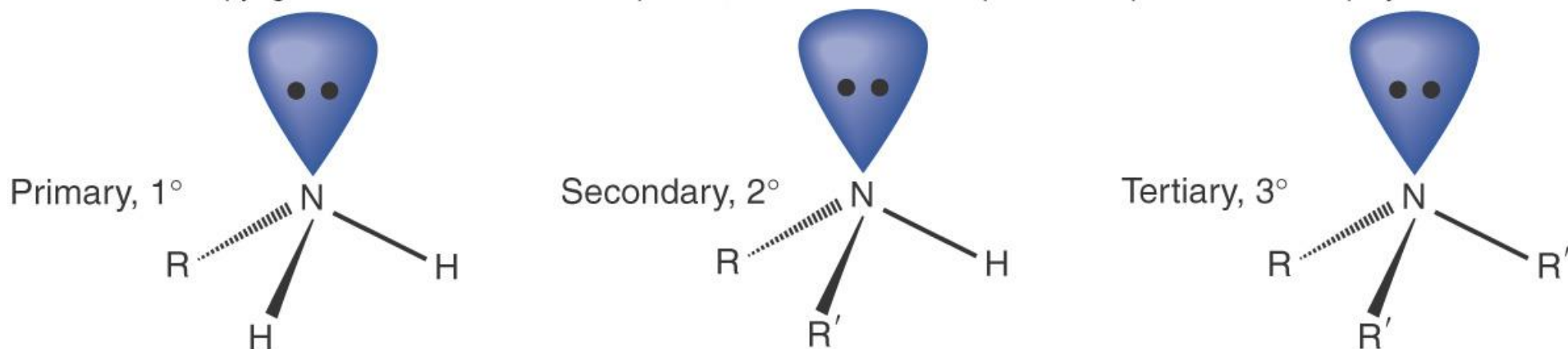
diethylamine

Amines



❖ General structures of amines.

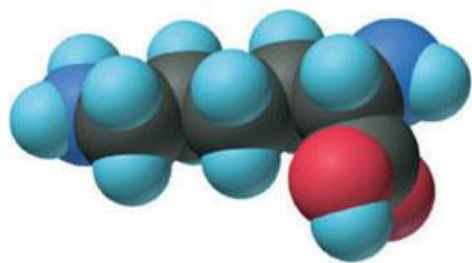
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❖ Amines are **classified** according to **the number of R groups directly** attached to the **N** atom.

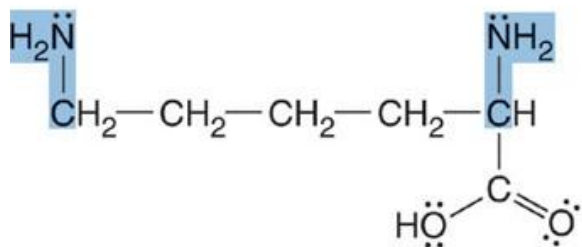
Amines

❖ Some biomolecules with the amine functional group.



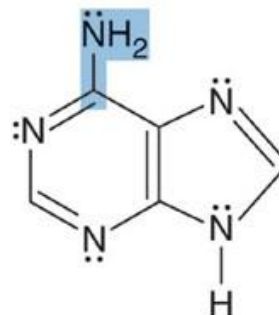
Lysine (1° amine)

amino acid found in proteins

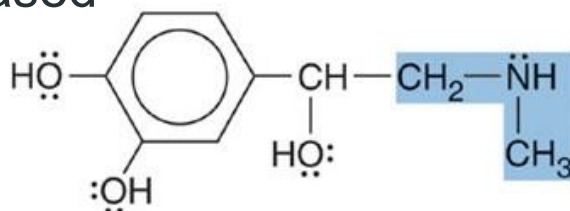
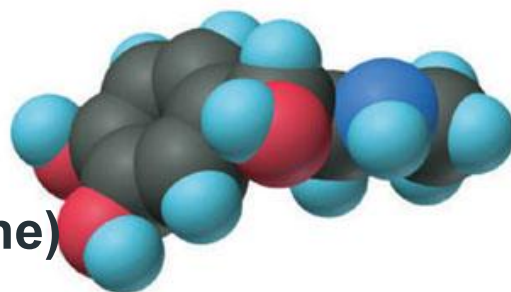


Adenine (1° amine)

component of nucleic acids

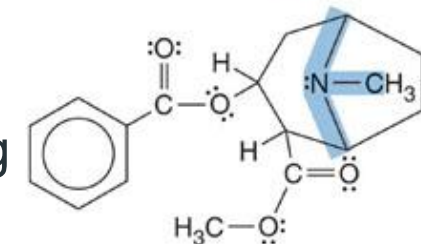


Epinephrine (adrenaline; 2° amine)
neurotransmitter in brain; hormone released during stress



Cocaine (3° amine)

brain stimulant; widely abused drug





Properties and Reactions of Amines

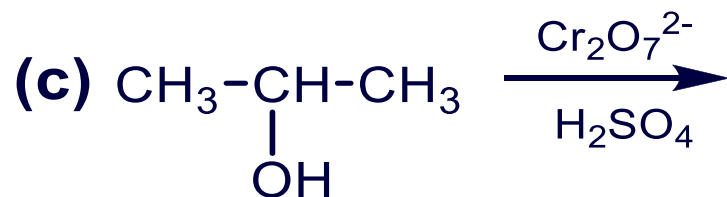
- Primary and secondary amines **can form H bonds**; therefore they have **higher** melting and boiling points than hydrocarbons or alkyl halides of similar mass.
- Tertiary amines **cannot form H bonds** between their molecules because they **lack a polar N–H bond**.
- Amines of low molar mass are fishy smelling, water soluble, and weakly basic.
- Amines undergo a variety of reactions, including **substitution** reactions.

Amines

Sample Problem

Predicting the Reactions of Alcohols, Alkyl Halides, and Amines?

PROBLEM: Determine the reaction type and predict the product(s) for each reaction:



PLAN We first **determine** the functional group(s) of the reactant(s) and then **examine** any inorganic reagent(s) to decide on the reaction type. Keep in mind that, in general, these functional groups undergo **substitution** or **elimination**.

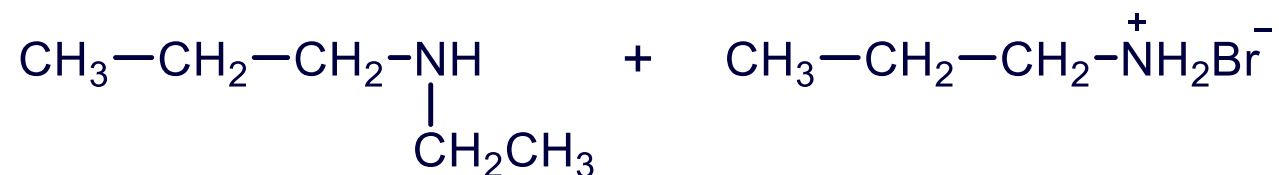
Amines

SOLUTION:

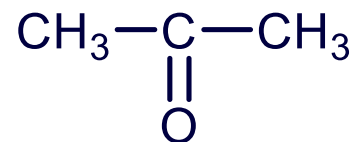
(a) In this reaction the OH of the NaOH reaction **substitutes** for the I in the organic reagent:



(b) This is a **substitution** reaction:



(c) This is an **elimination** reaction since acidic $\text{Cr}_2\text{O}_7^{2-}$ is a strong oxidizing agent:



Amides

An amide contains the functional group:

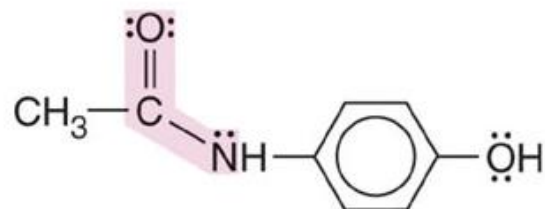
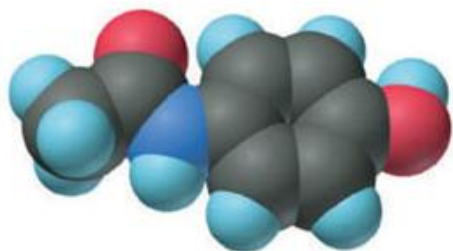


Amides, like esters, can be hydrolyzed to give a carboxylic acid and an amine.

The ***peptide bond***, which links amino acids in a protein, is an amide group.

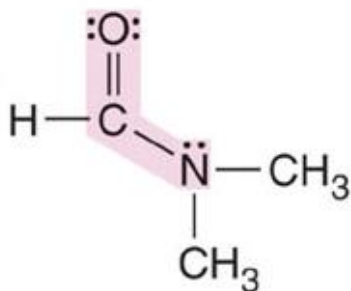
Amides

❖ Some molecules with the amide functional group.



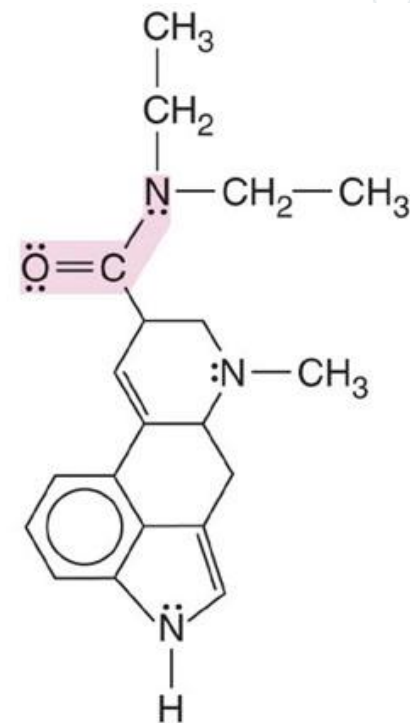
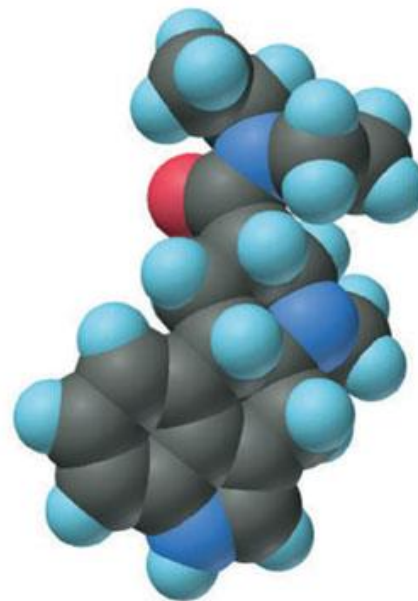
Acetaminophen

Active ingredient in nonaspirin pain relievers; used to make dyes and photographic chemicals



N,N-Dimethylmethanamide (dimethylformamide)

Major organic solvent; used in production of synthetic fibers

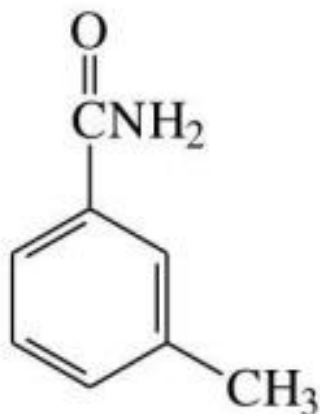


Lysergic acid diethylamide (LSD-25)

A potent hallucinogen

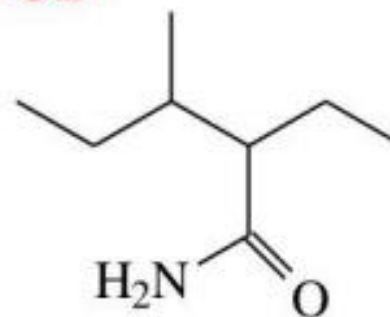
Amides

❖ Some molecules with the amide functional group.

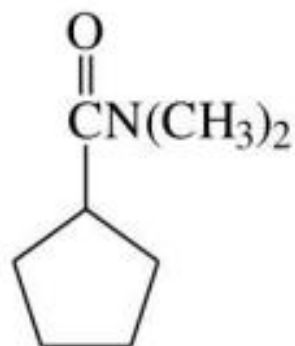


meta methylbenzamide

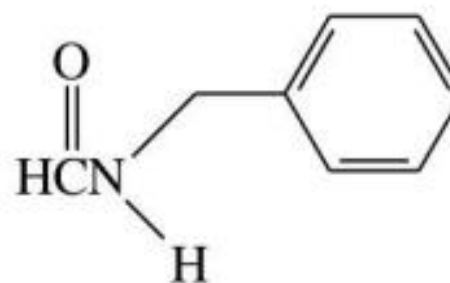
Amides



2-ethyl-3-methylpentanamide
 α -ethyl- β -methyl valeramide



N,N-dimethylcyclopentanecarboxamide

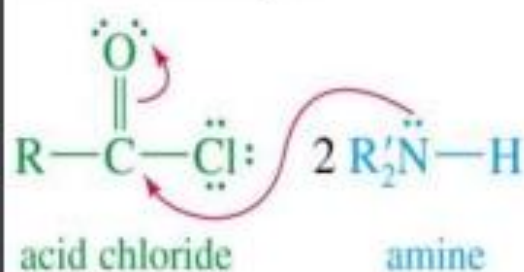


N-benzylformamide

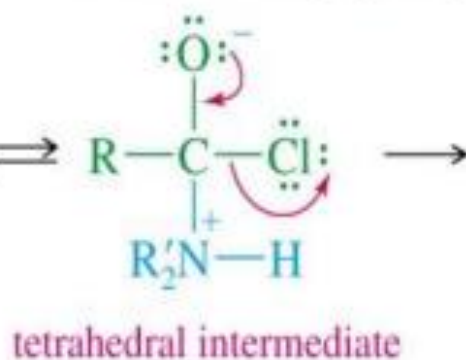
Amides

Amide Preparation from an Acid Chloride

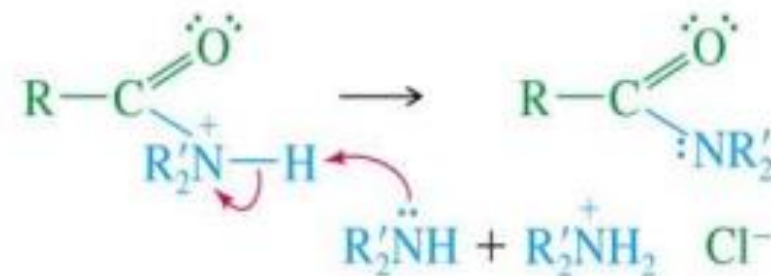
*Step 1: Addition
of the nucleophile*



*Step 2: Elimination
of the leaving group*



Step 3: Loss of a proton



Amines and Amides

How to name amines/amides

Amines

- Count parent carbon chain
- Assign locant to amine (lowest #)
- Name of a normal hydrocarbon
- Drop “e”
- Add “amine”
- Put locant in front

Amides

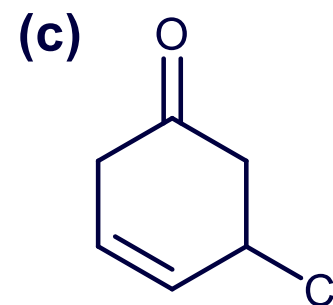
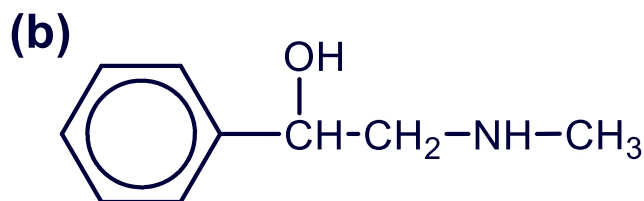
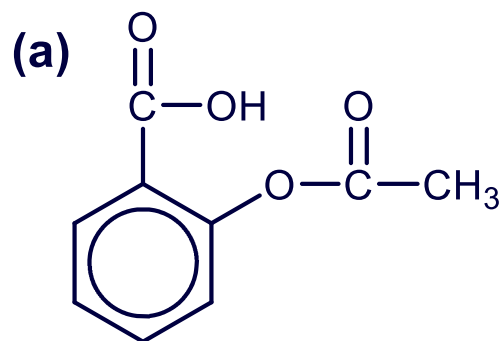
- Count parent carbon chain
- Name of a normal hydrocarbon
- Drop “e”
- Add “amide”

Amines

❖ Sample Problem

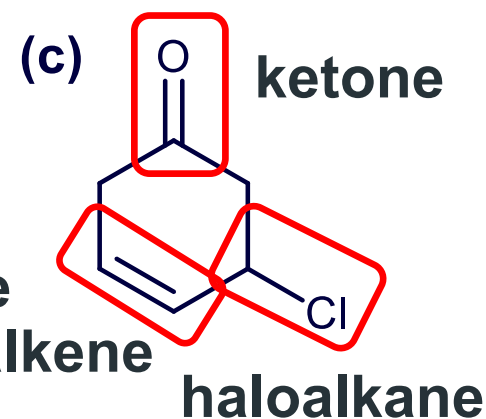
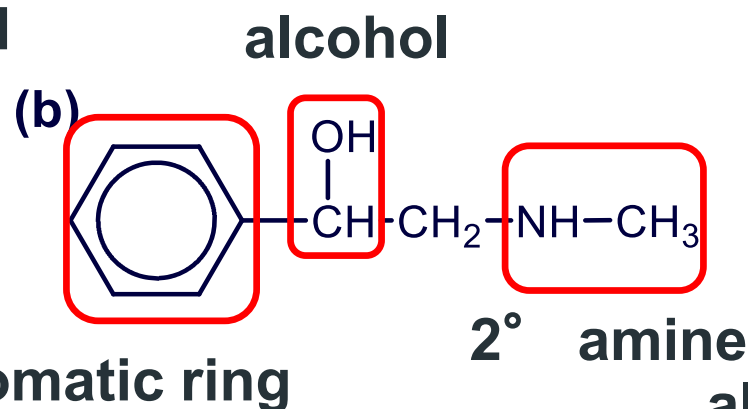
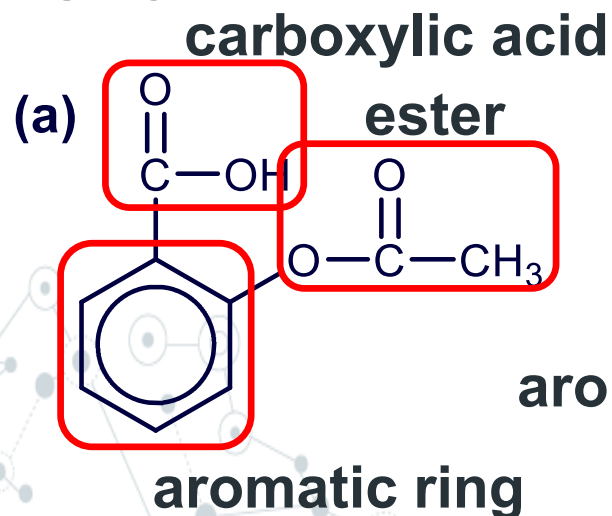
Recognizing Functional Groups?

PROBLEM: Circle and name the functional groups in the following molecules:



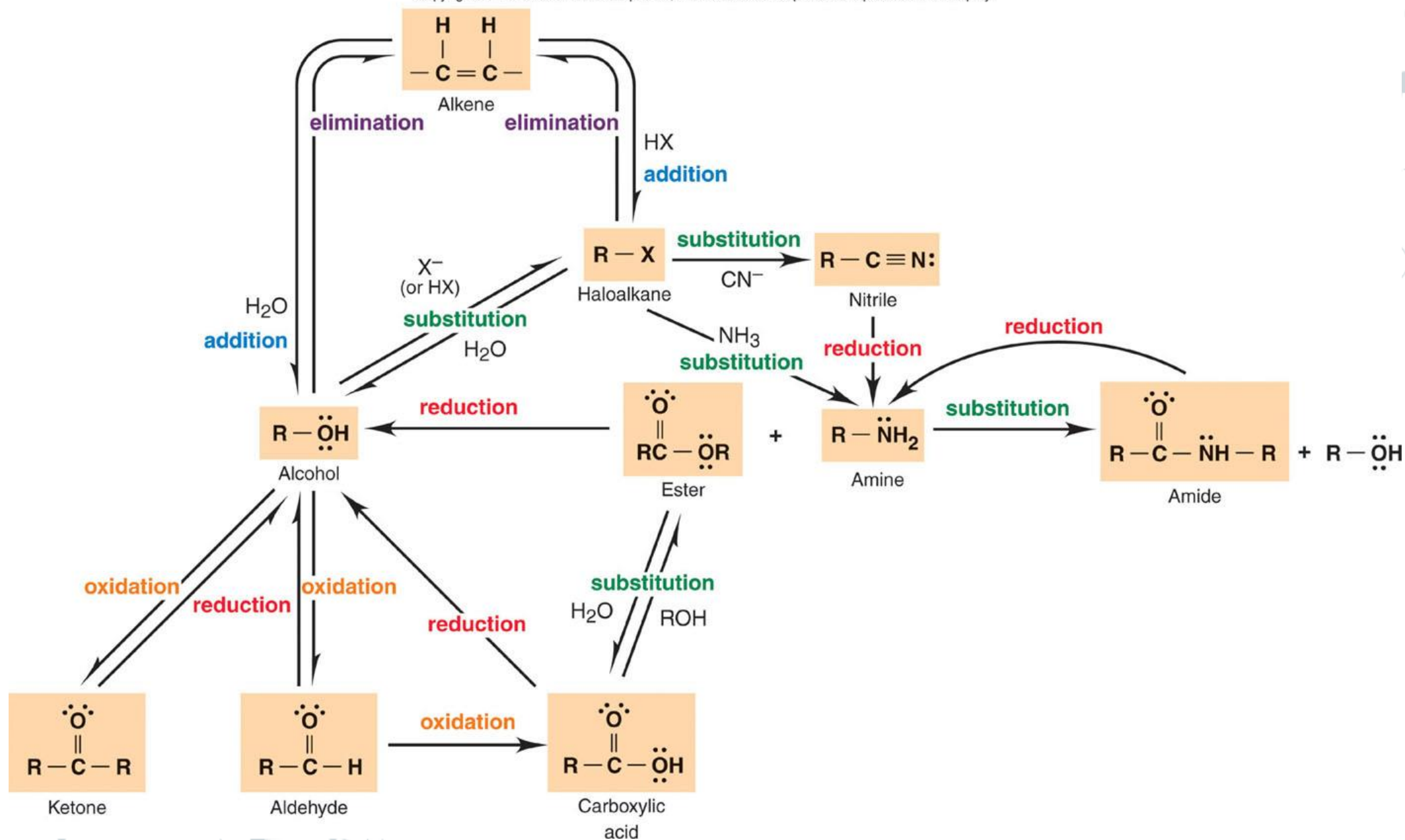
PLAN: Use Table of functional group to identify the various functional groups.

SOLUTION:



A summary of the interconversions among the major organic functional groups

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**THE
END**