كلية العلوم التطبيقية
Faculty of Applied Sciences

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Organic chemistry (1)
402232-3

(Integrated course in plane 36 for 6 groups in second term 1437-1438H)

Hydrocarbons

Hydrocarbons

Introduction:

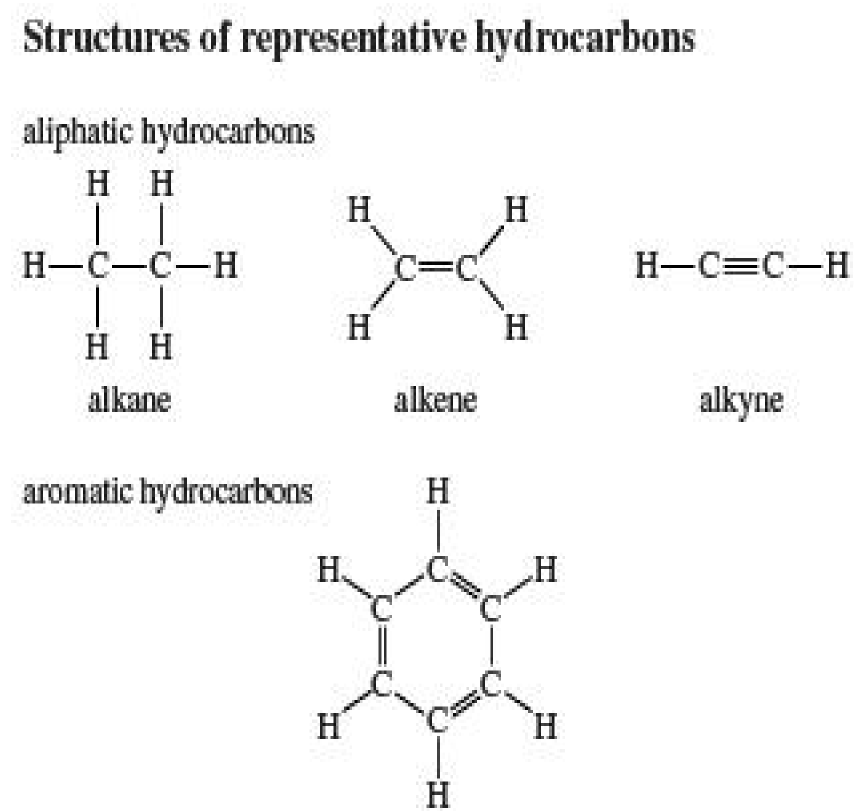
- A large group of organic compounds, known as hydrocarbons, contain only the two elements: carbon and hydrogen. Based on their structural features.

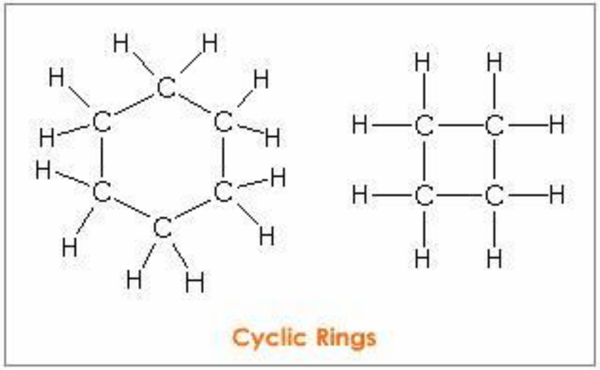
- They are divided into two main classes: aliphatics and aromatics.

- Aliphatic hydrocarbons are subdivided into three families:

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

alkenes and alkynes (unsaturated hydrocarbons).





Definitions, classification, characterizations and general formula

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

- **Aliphatic:**

a) Saturated hydrocarbons:

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

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

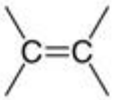
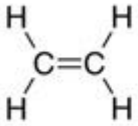
b) Unsaturated hydrocarbons:

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

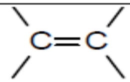
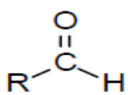
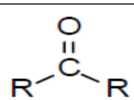
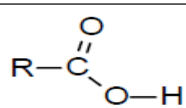
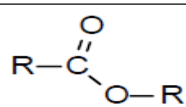
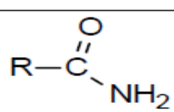
➢ **Alkynes** (C_nH_{2n-2}) contain at least one carbon–carbon triple bond. They formed in open chain with general formula C_nH_{2n-2}. Also formed in cyclic chain with general formula C_nH_{2n-4}

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

General structure of hydrocarbons

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

Organic Functional Group List

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

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

Alkanes

Alkanes and Cycloalkanes

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

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

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

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

They are categorized as acyclic or cyclic.

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

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

Aliphatics
Saturated hydrocarbons: Alkanes

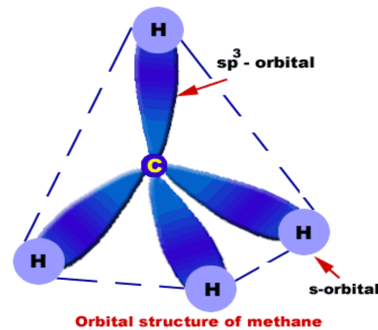
Saturated hydrocarbons (alkanes=paraffins):

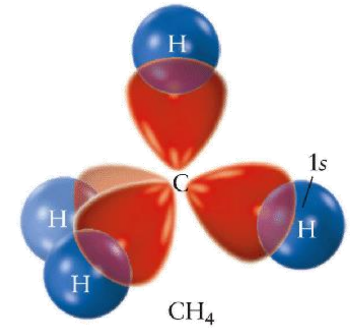
The three simplest alkanes (Methane, ethane and propane):

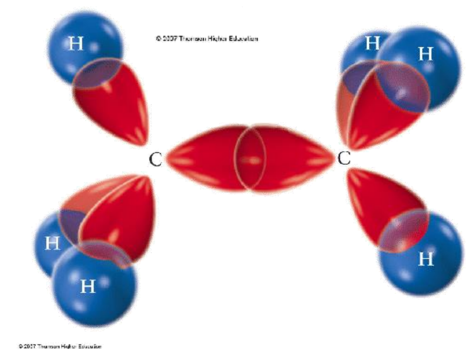
1- Methane CH_4 has the shape of a tetrahedron with an sp^3-hybridized orbitals, carbon at the center. All four C-H bonds in the molecule are equivalent.

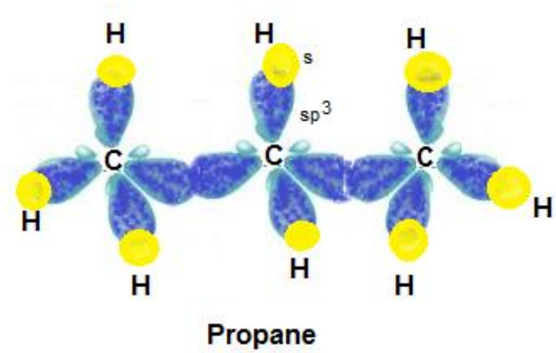
2- Ethane C_2H_6 is more than methane with alkyl group (CH_2). Each carbon in ethane is *sp3* hybridized orbitals and the bond joining the two carbons is called an *sp3-sp3* molecular orbital.

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



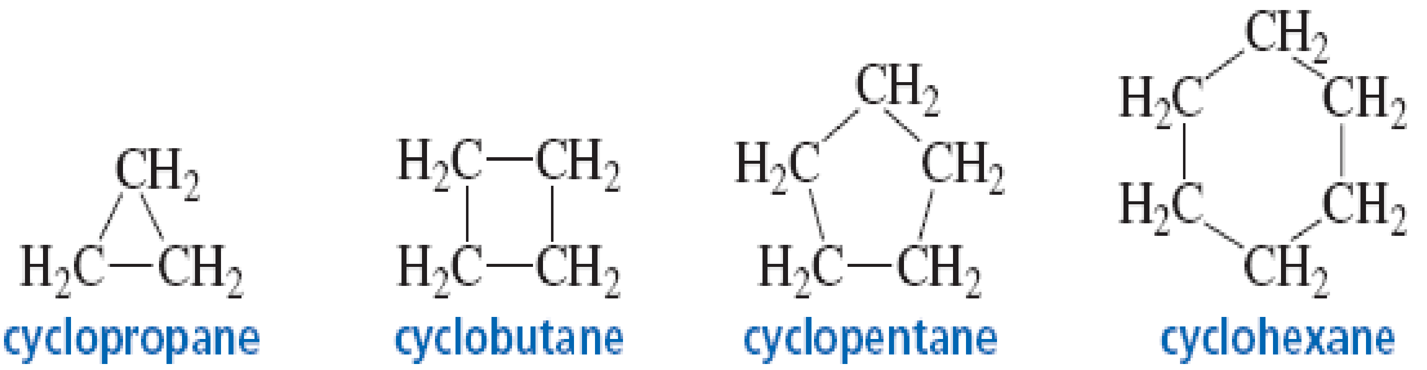






Structure of Cycloalkanes

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



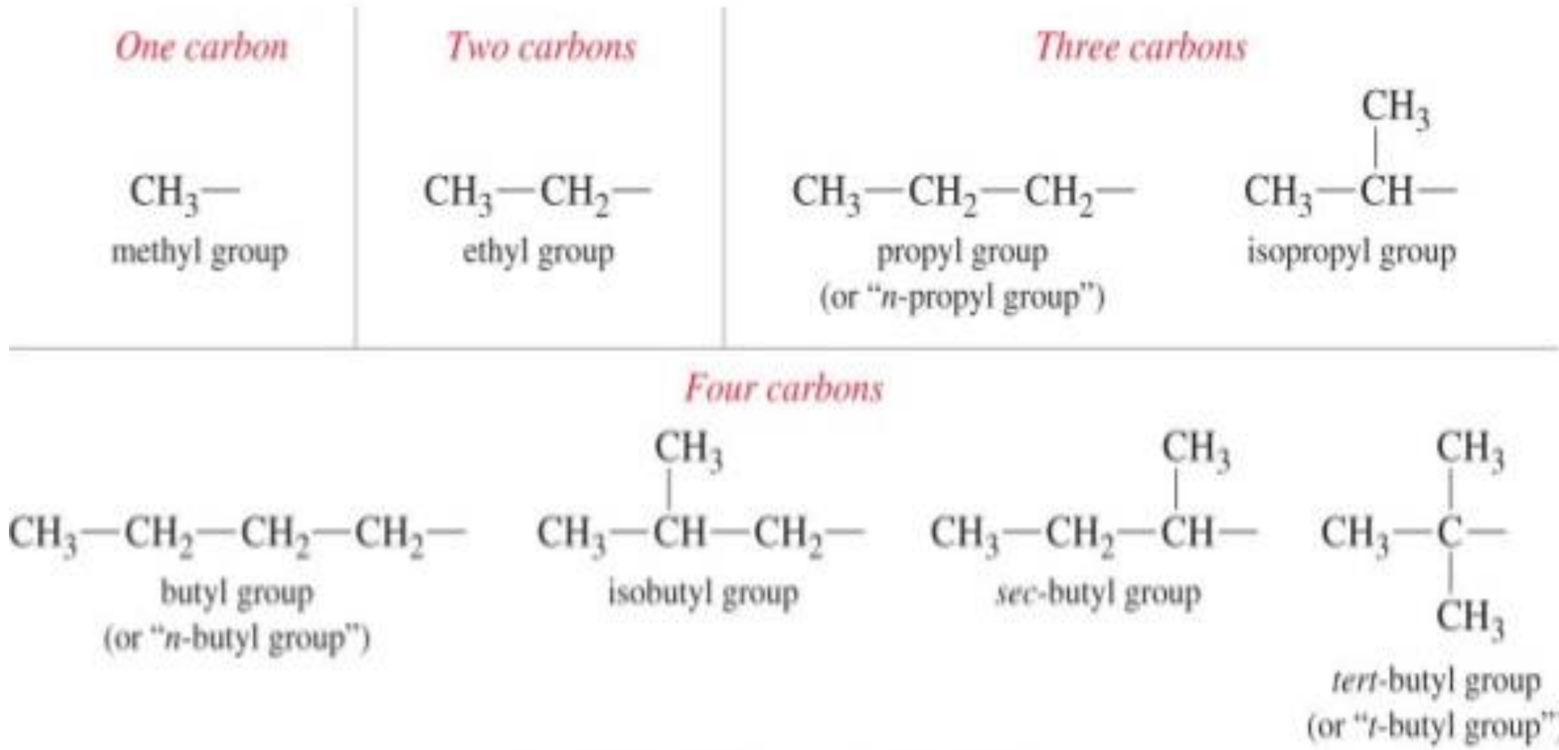
Naming Alkanes

The suffix "-ane" identifies a molecule as an alkane.

Summary: Straight-Chain Alkanes

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

Common Alkyl Groups



Sources of alkanes

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

Physical Properties of Alkanes

1- Solubility:

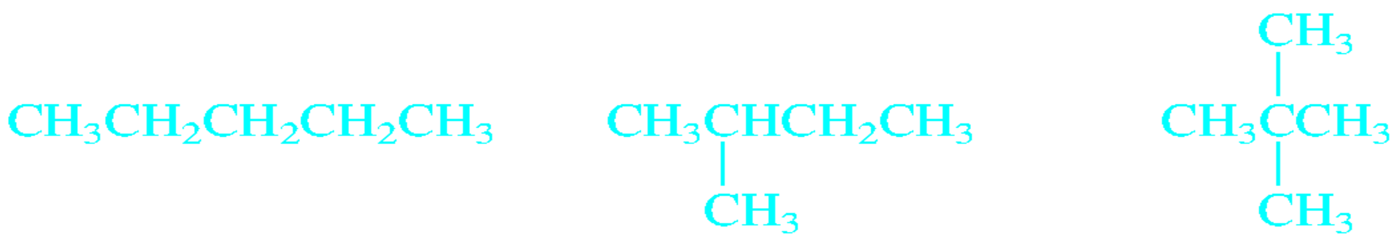
- Alkanes occur at room temperature as gases, liquids and solids.
- Alkanes from C_1 to C_4 are gases; most C_5 to C_{17} alkanes are liquids and the C_{18} and larger alkanes are wax-like solid. (The first four alkanes in homological row are gaseous at room temperature. The unbranched alkanes pentane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

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

Physical Properties of Alkanes

2- Boiling point:

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



Pentane (bp 36°C) | 2-Methylbutane (bp 28°C) | 2,2-Dimethylpropane (bp 9°C)

3- Melting point:

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

4- Density:

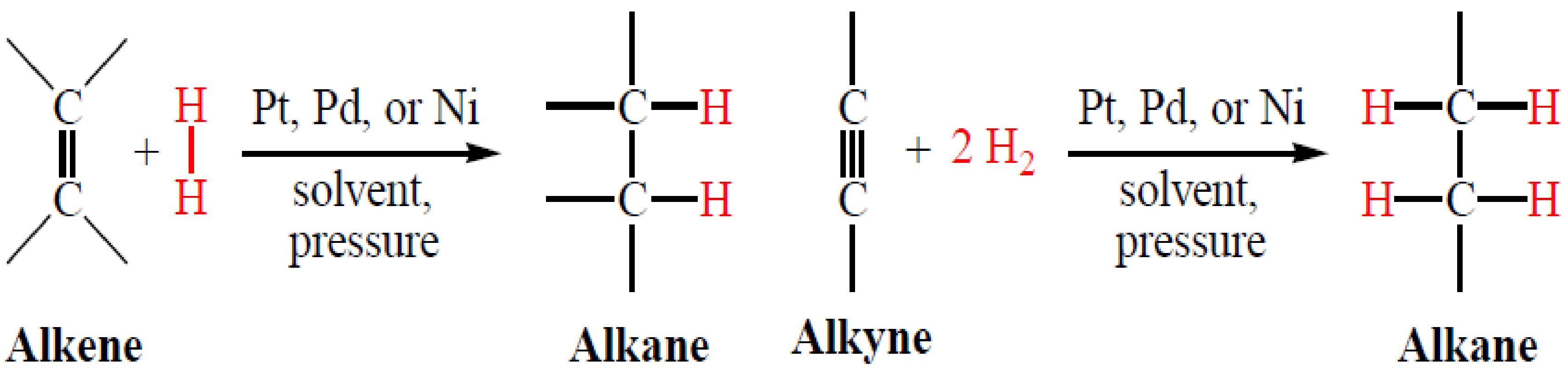
The alkanes are the least dense of all groups of organic compounds.

Preparation of Alkanes and Cycloalkanes

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

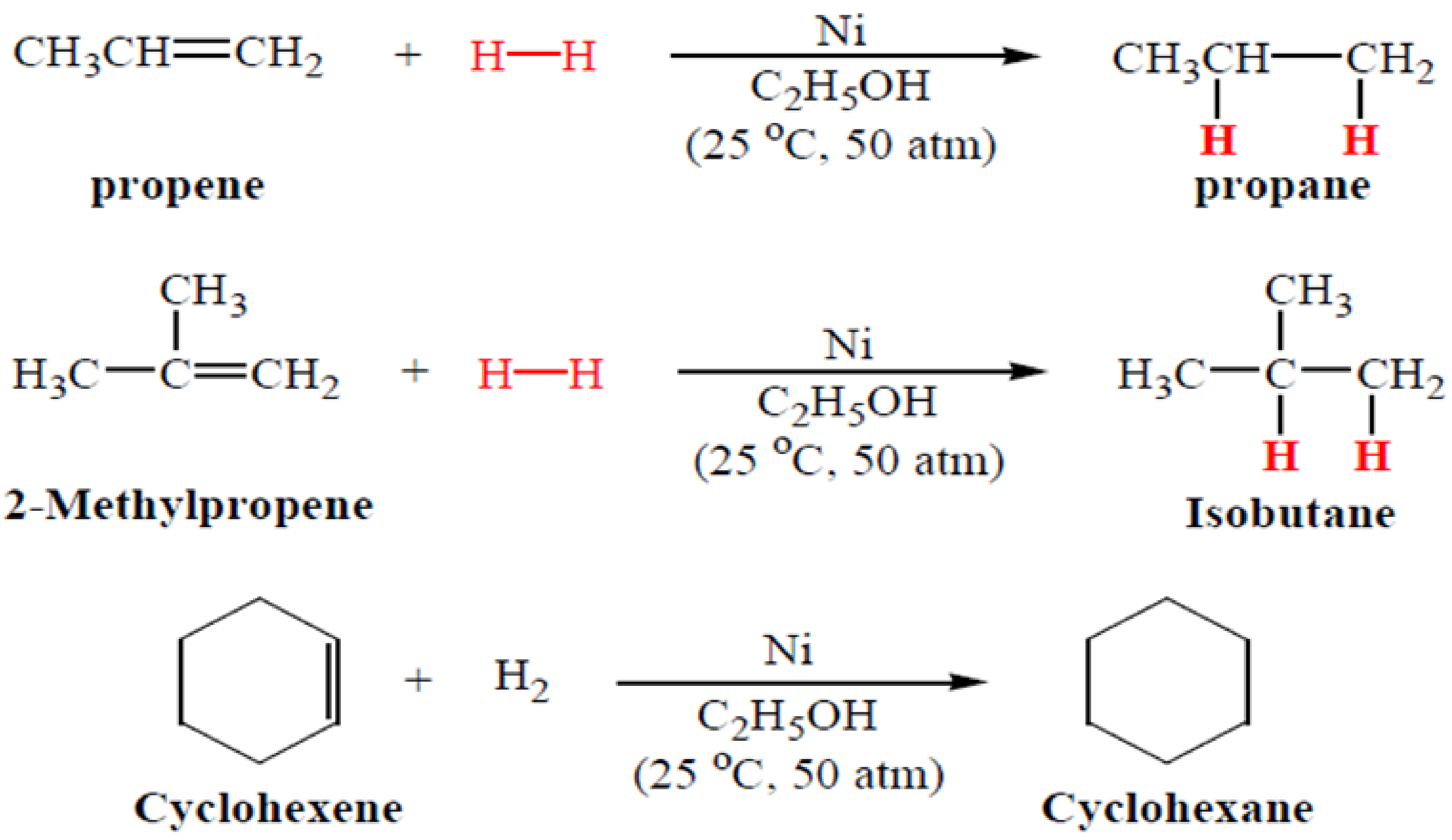
Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce alkanes.

General Reaction:



Preparation of Alkanes and Cycloalkanes

Examples:



Preparation of Alkanes and Cycloalkanes

2- Reduction of alkyl halides:

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

General Reaction:

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

or*

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

Example:

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

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

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

Isopentyl bromide (1-bromo-3-methylbutane) → **Isopentane (2-methylbutane)**

Preparation of Alkanes and Cycloalkanes

3- Wurtz reaction (Alkyl halides via coupling):

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

General Reaction:

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

Example:

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

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

Preparation of Alkanes and Cycloalkanes

4- Alkyl halides via Grignard reagent:

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

$$\underset{\substack{(X = Cl,\ Br,\ or\ I) \\ \text{Alkyl halide}}}{R{-}X} + Mg \xrightarrow[\text{Dry ether}]{CH_3CH_2OCH_2CH_3} \underset{\substack{\text{organomagnesium halide} \\ \text{(Grignard reagent)}}}{\overset{\delta-}{R}{-}\overset{\delta+}{Mg}{-}X}$$

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

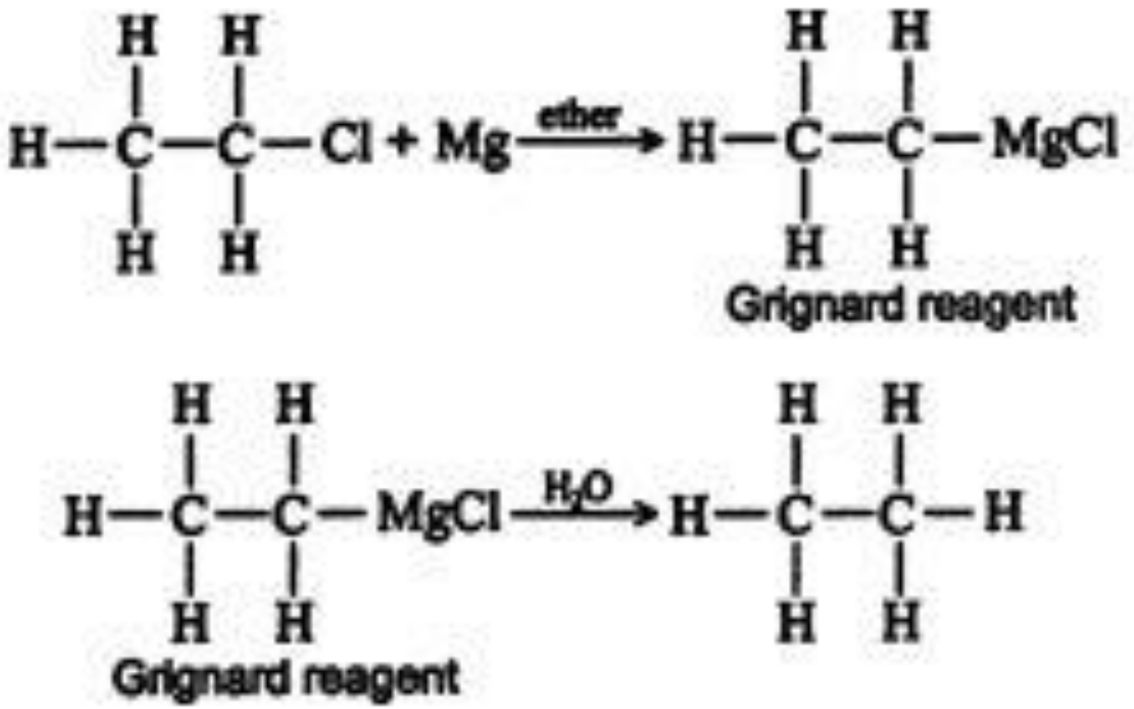
$$R\text{-}MgX \xrightarrow{H_2O} \underset{\text{Alkane}}{R\text{-}H} + Mg(OH)X$$

General reaction:

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

Preparation of Alkanes and Cycloalkanes

Example:



Ethane

Preparation of Alkanes and Cycloalkanes

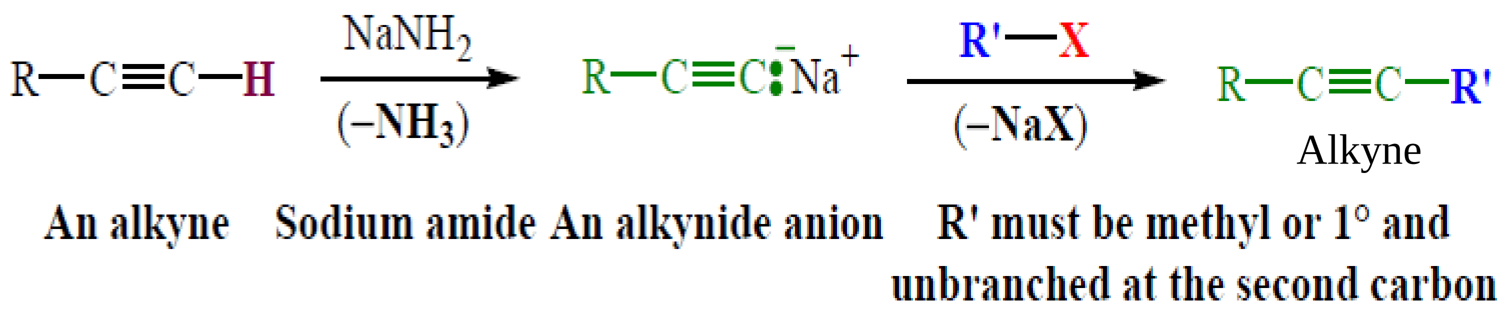
5- Alkylation of terminal alkynes:

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

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

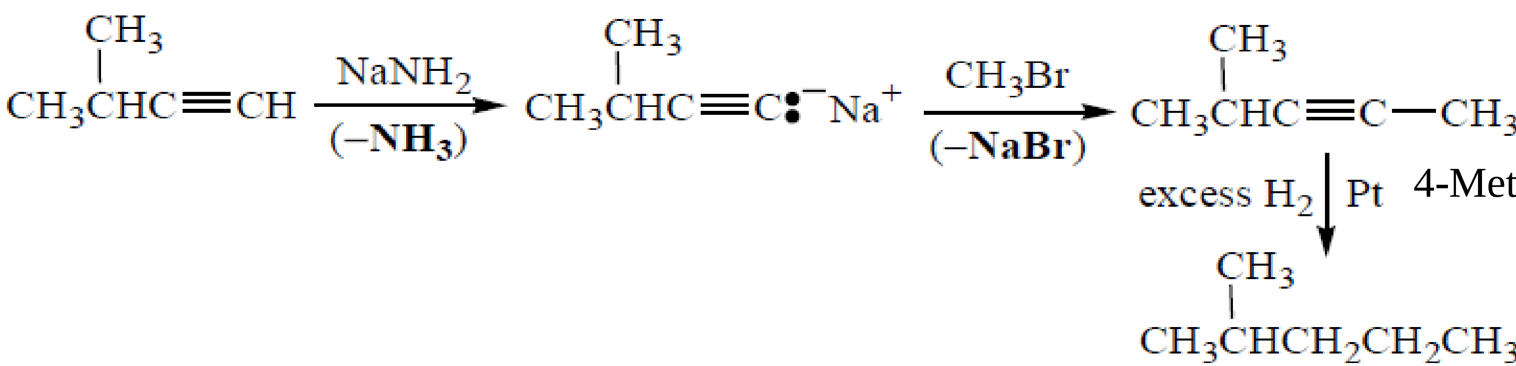
2. Alkylation: the **formation of a new C—C bond** by replacing a **leaving group** on an **electrophile** with a **nucleophile**.

General Reaction:



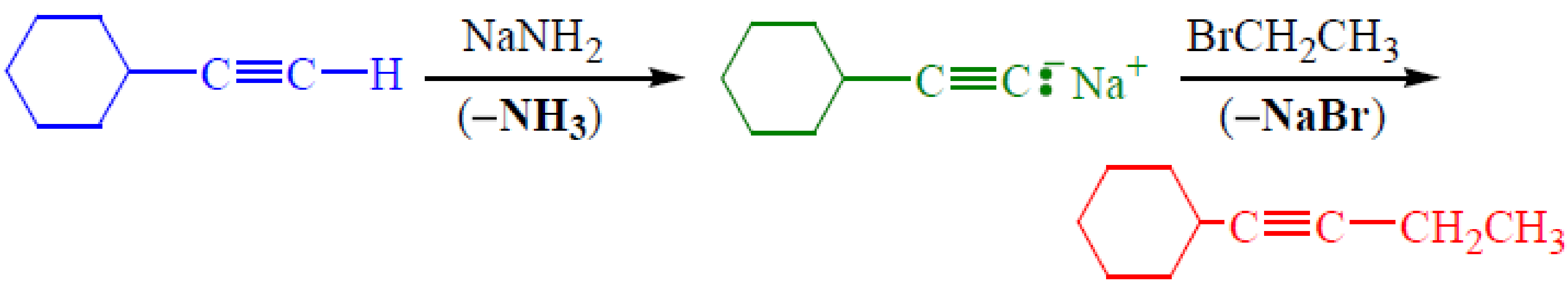
Preparation of Alkanes and Cycloalkanes

Example:



4-Methyl,2-pentyne

2-Methylpentane
Isohexane



1-Cyclohexyl,1-butyne

Chemical properties of Alkanes

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

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

Reaction of alkanes

1- Halogenation:

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

$$\underset{\text{Methane}}{CH_4} + Cl_2 + \text{energy} \longrightarrow \underset{\textbf{methyl chloride}}{CH_3Cl} + HCl$$

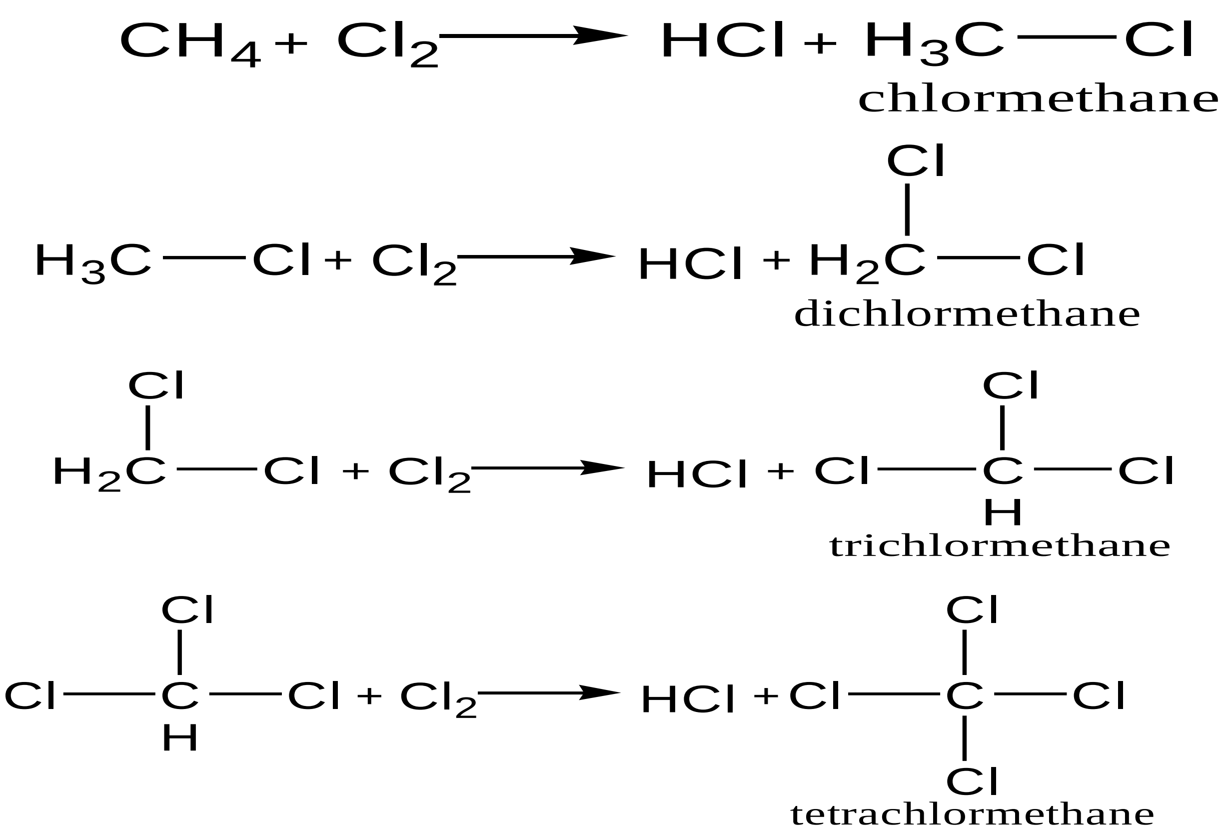
- Since only two covalent bonds are broken (C-H & Cl-Cl) and two covalent bonds are formed (C-Cl & H-Cl).
- In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.

$$\underset{\text{Methane}}{CH_4} + Cl_2 + \text{energy} \longrightarrow \underset{\textbf{methyl chloride}}{CH_3Cl} + \underset{\textbf{dichloromethane}}{CH_2Cl_2} + \underset{\textbf{chloroform}}{CHCl_3} + \underset{\textbf{carbon tetrachloride}}{CCl_4} + HCl$$

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

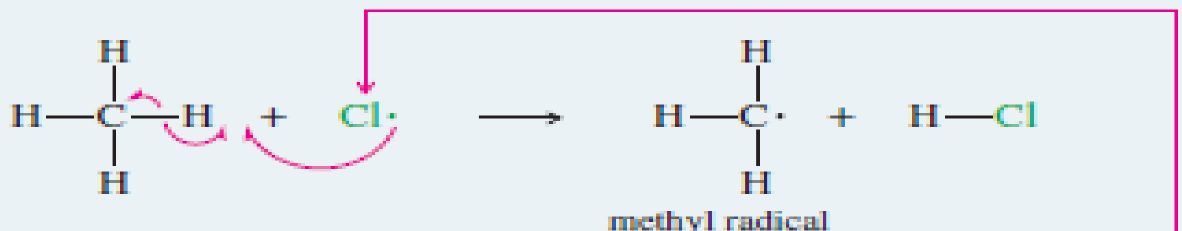
Steps of halogenation:

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



Initiation: Radicals are formed.
Light supplies the energy to split a chlorine molecule.

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



continues the chain

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

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

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

Reaction of alkanes

2- Combustion:

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

$$C_nH_{2n+2} + 3n+1/2\ O_2 \longrightarrow n\,CO_2 + (n+1)\,H_2O + \text{heat}$$

Alkane — Carbondioxide — Water

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

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

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

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

Propane — Carbonmonoxide

Reaction of alkanes

3- Nitration of alkanes:

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

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

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

4- Cracking of alkanes:

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

$$\underset{\text{Ethane}}{\mathbf{CH_3{-}CH_3}} \rightarrow \underset{\text{Ethene}}{\mathbf{CH_2{=}CH_2}} + \mathbf{H_2}$$

$$\mathbf{2\ \underset{\text{Butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} \rightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Propene}}{CH_2{=}CH{-}CH_3} + \underset{\text{Ethane}}{CH_3{-}CH_3} + \underset{\text{Ethene}}{CH_2{=}CH_2}}$$

Alkenes

Aliphatics

Unsaturated hydrocarbons: Alkenes

- Unsaturated hydrocarbons (Alkenes):

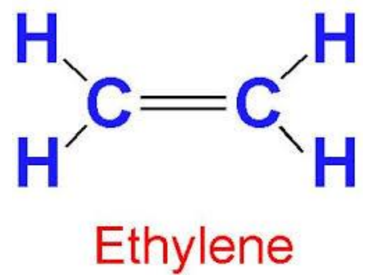
1- They are hydrocarbons contain fewer hydrogens than do alkanes having the same number of carbon atoms.

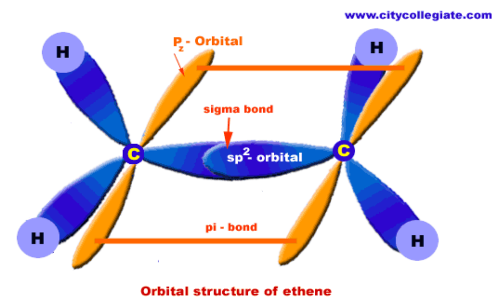
2-These compounds are deficient in hydrogen that why called unsaturated.

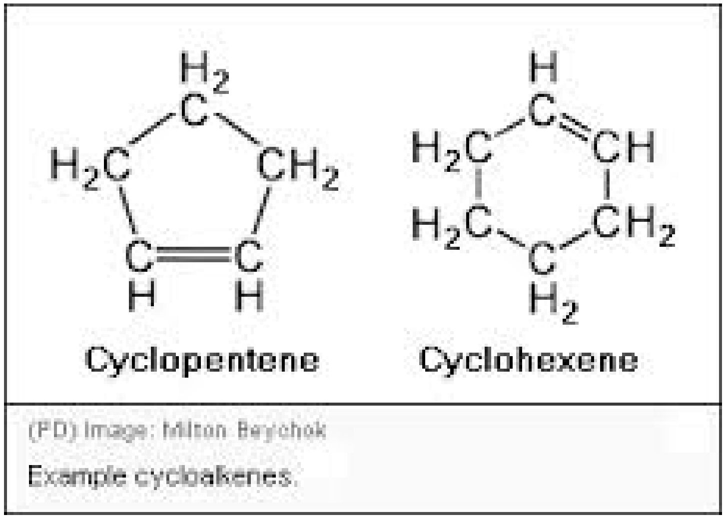
3- Characterized by: the presence of a carbon-carbon double bonds is called the alkenes and has the general formula C_nH_{2n}

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

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

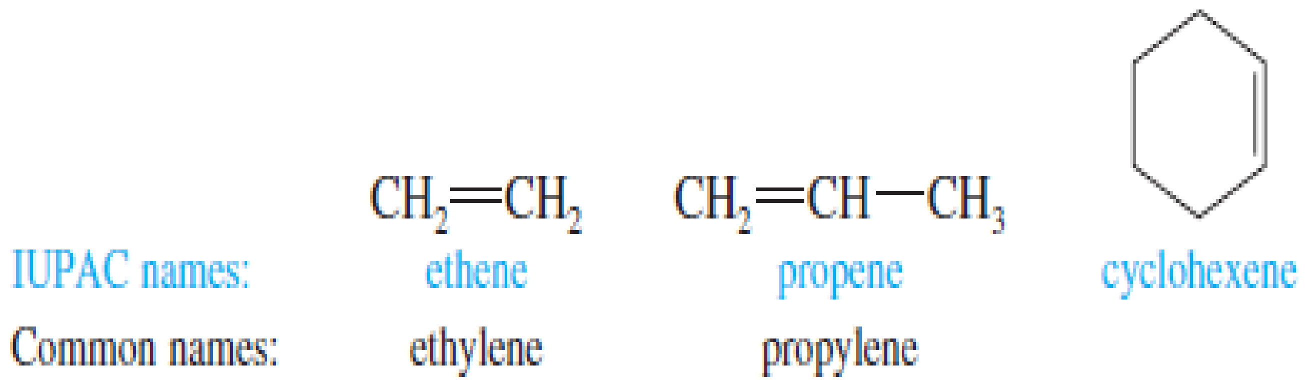






Alkene

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



Physical properties of alkenes

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

1. **Solubility & Polarity:**

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

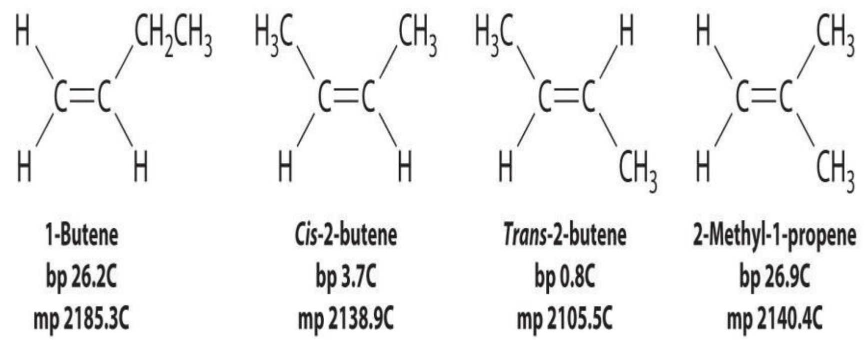
2. **Boiling point:**

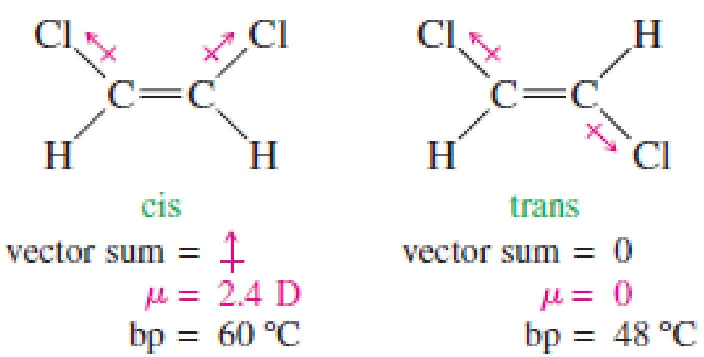
The boiling points of alkenes increase smoothly with molecular weight. As with alkanes, increased branching leads to greater volatility and lower boiling points.

Physical properties of alkenes

3. Geometric isomerism in alkenes:

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

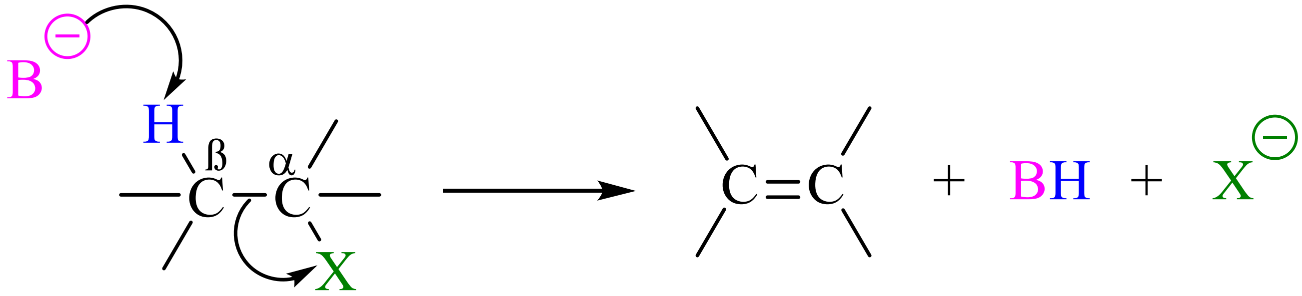




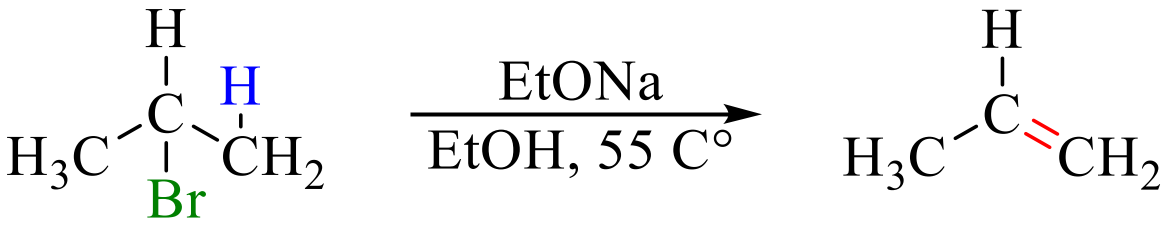
Preparation of Alkenes

1. Dehydrohalogenation of alkyl halides

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



Examples:

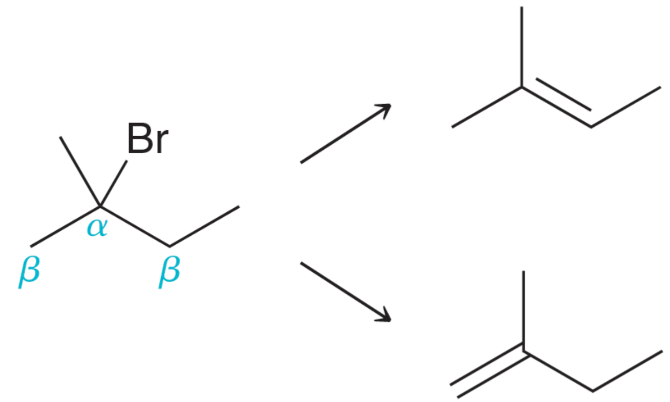


2-bromopropane

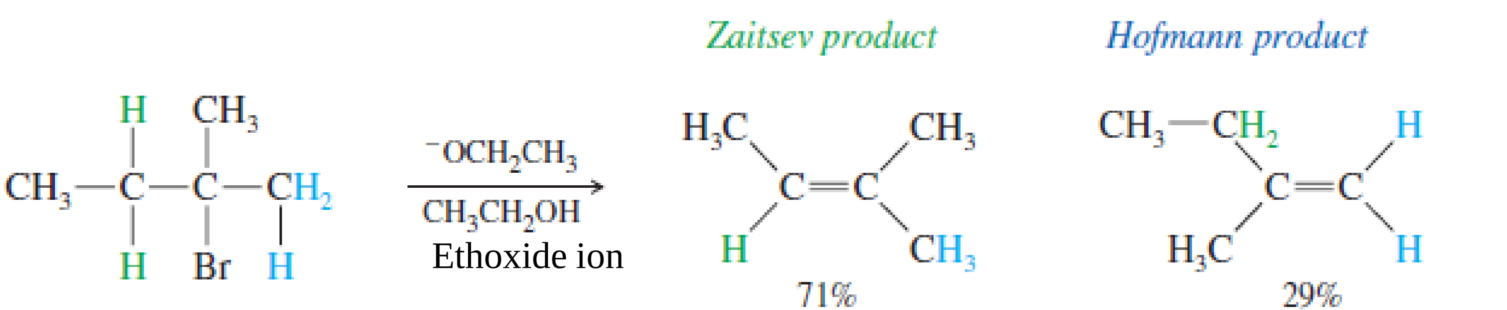
prop-1-ene

Preparation of Alkenes

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



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



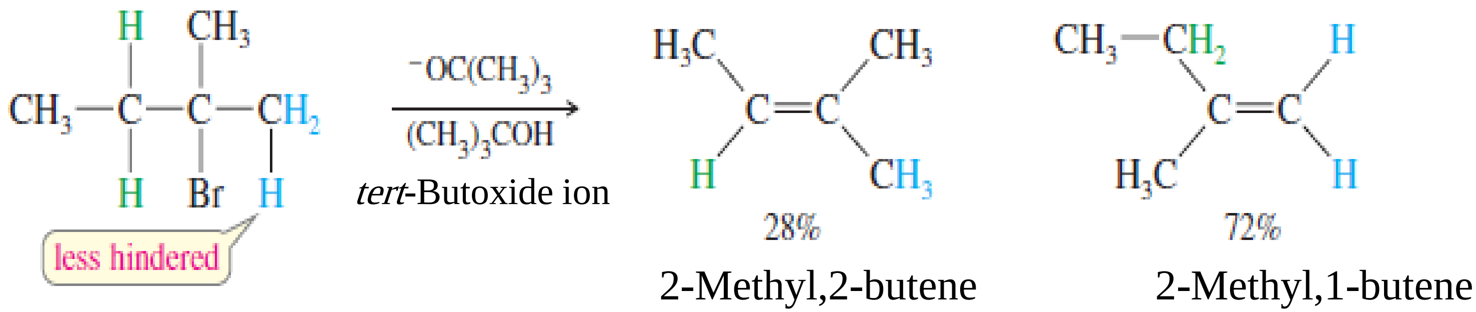
2-Bromo,2-methylbutane

2-Methyl,2-butene

2-Methyl,1-butene

Preparation of Alkenes

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



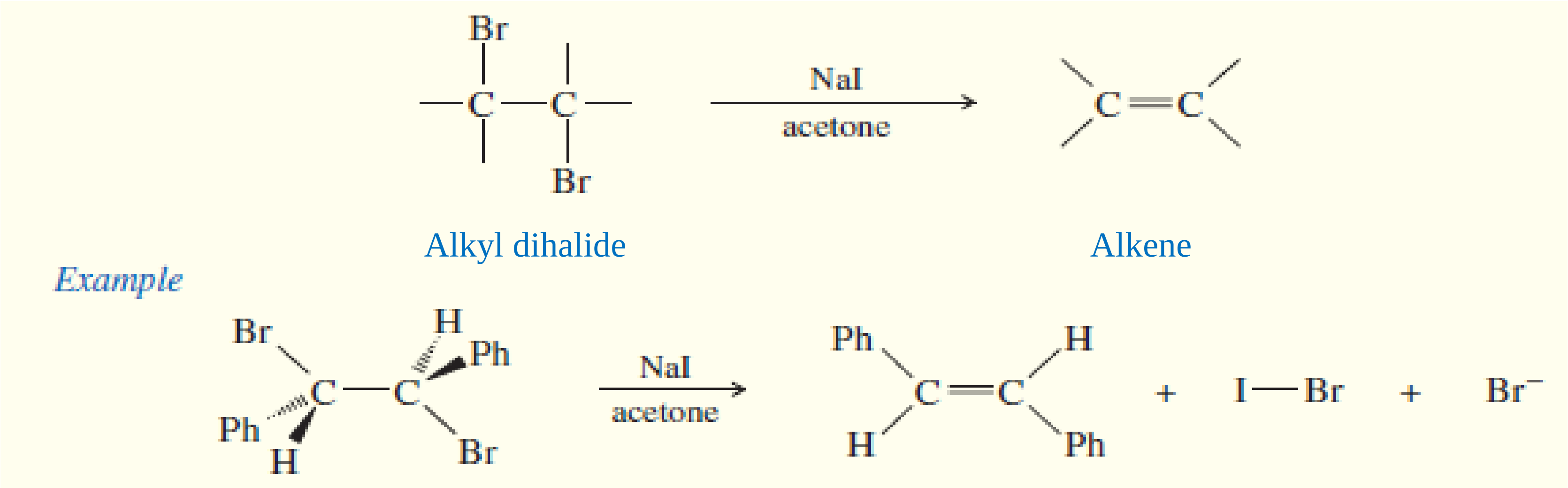
Zaitsev's Rule: The formation of the more substituted alkene is favoured with small bases.

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

Preparation of alkenes

2. Dehalogenation of vicinal dibromides:

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

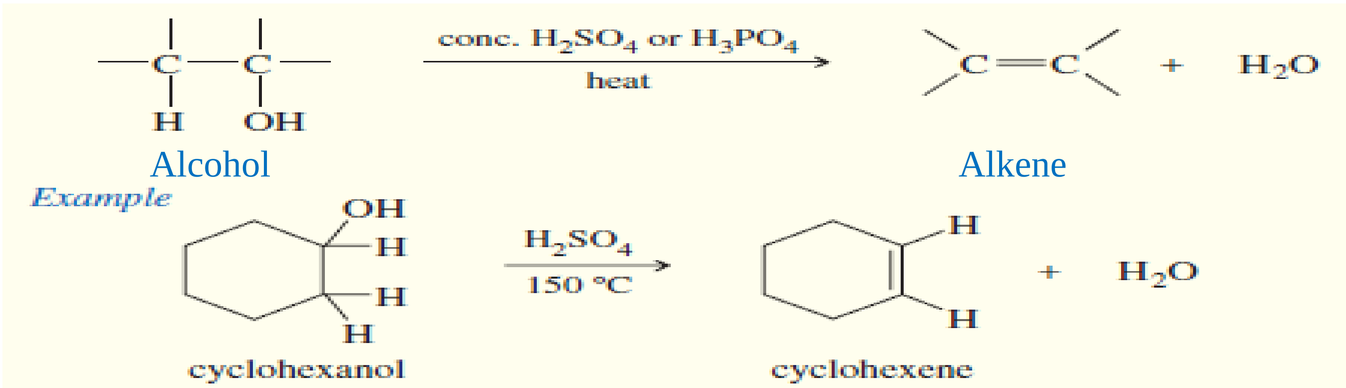


1,2-Dibromo,1,2-diphenyl,ethane trans-1,2 diphenylethene

Preparation of Alkenes

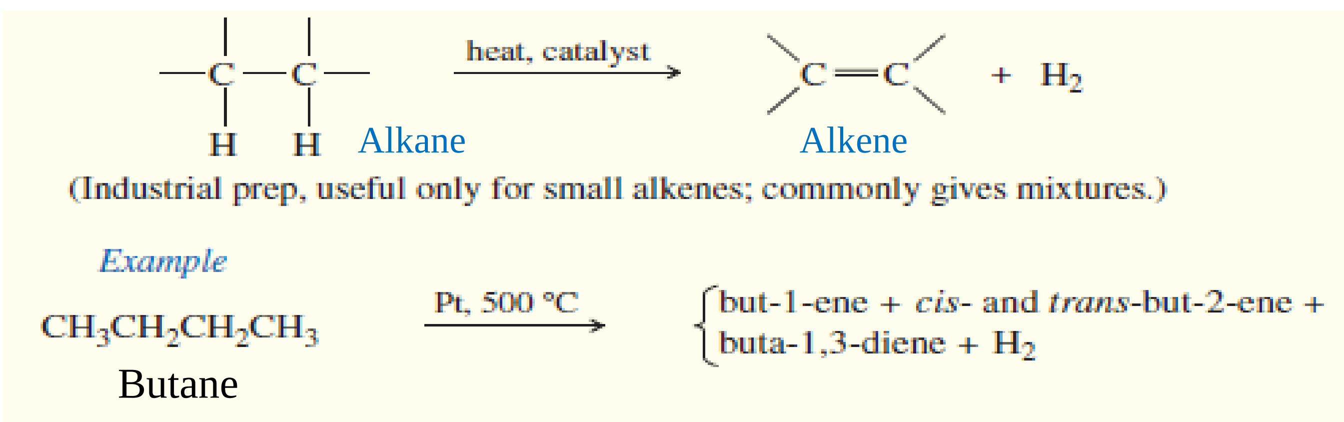
3. Dehydration of alcohols:

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



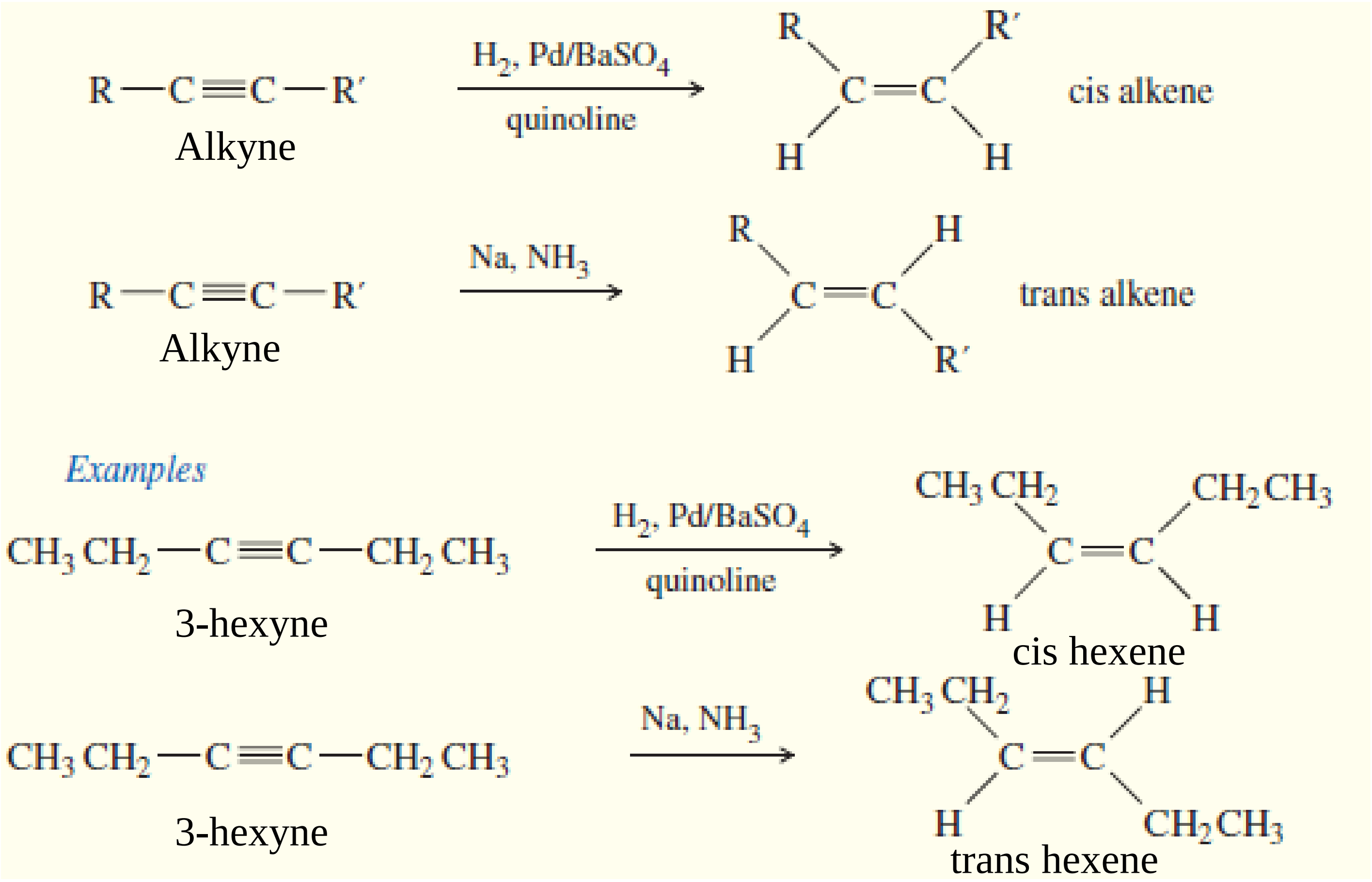
4. Dehydrogenation of alkanes:

Dehydrogenation is the removal of H_2 from a molecule.



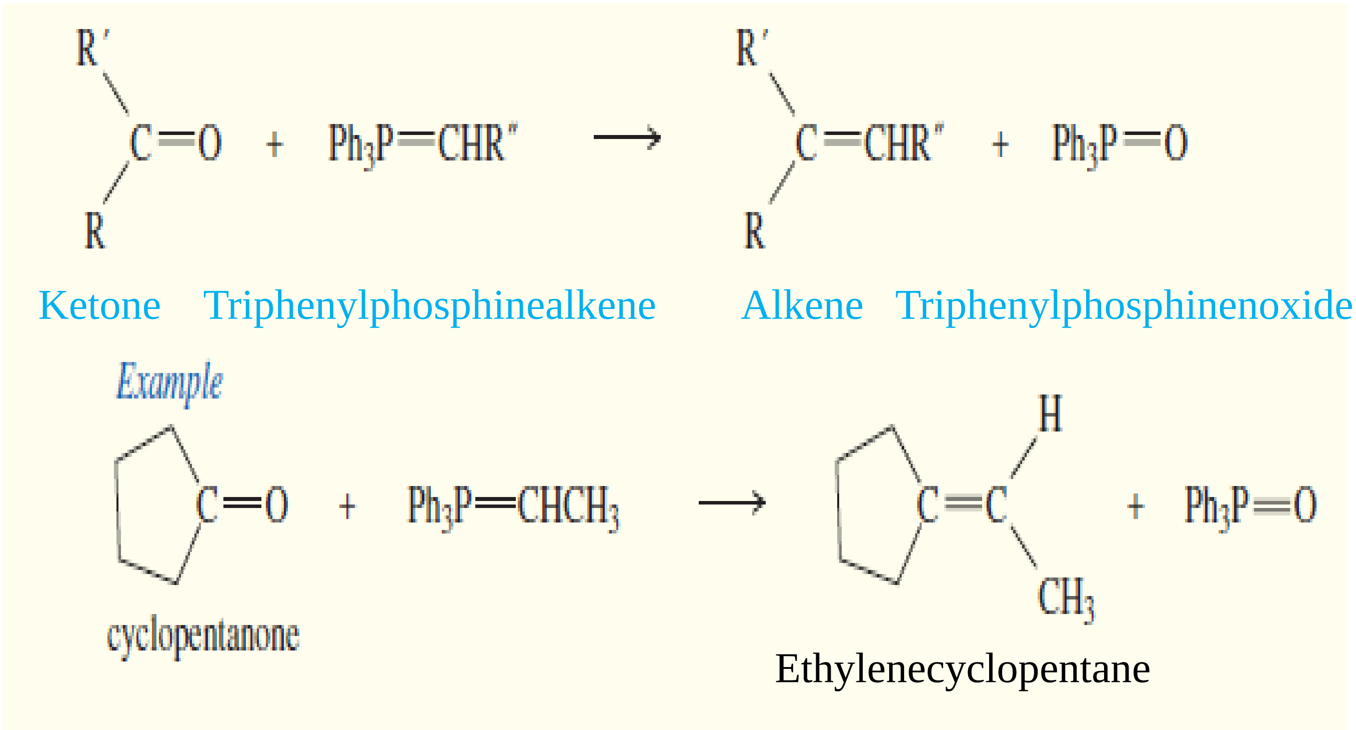
Preparation of Alkenes

5-Reduction of alkynes:



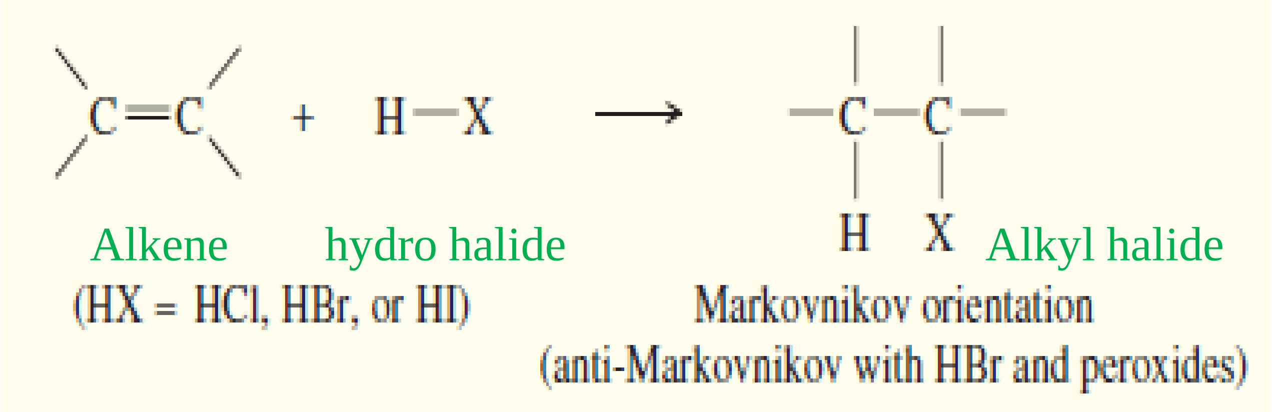
Preparation of Alkenes

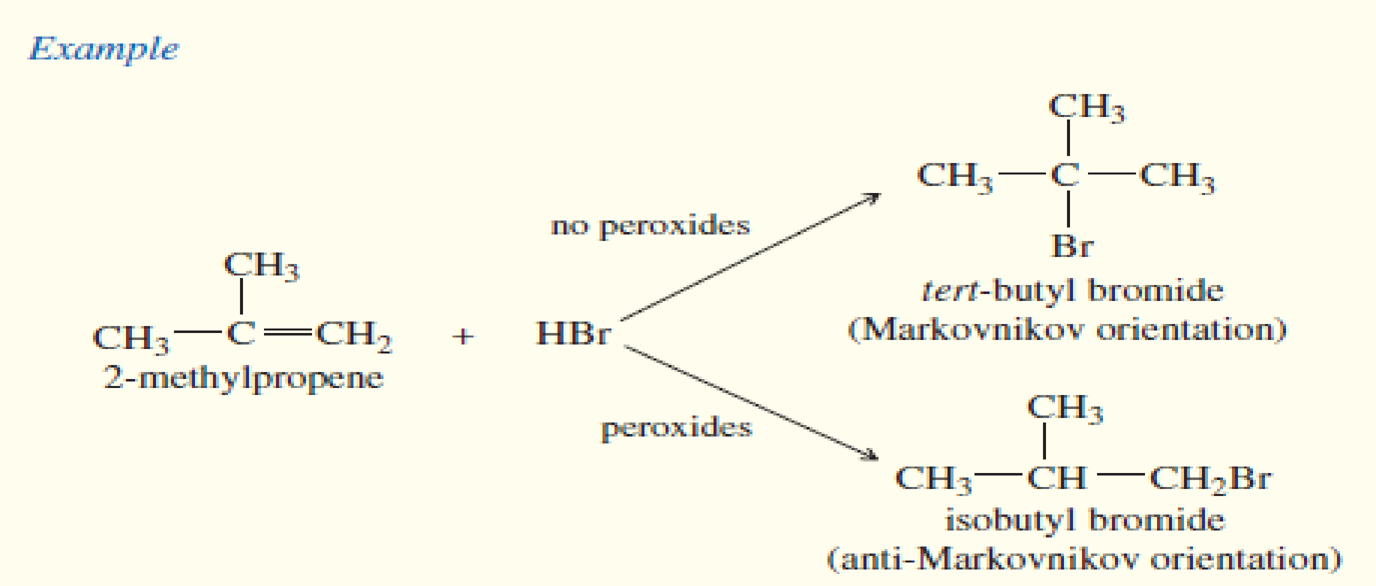
6-Wittig reaction:



Reaction of Alkenes

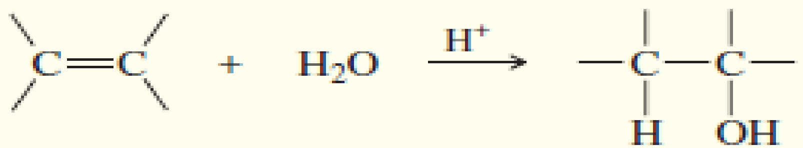
1- Addition of hydrogen halides:





Reaction of Alkenes

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



Alkene

Alcohol

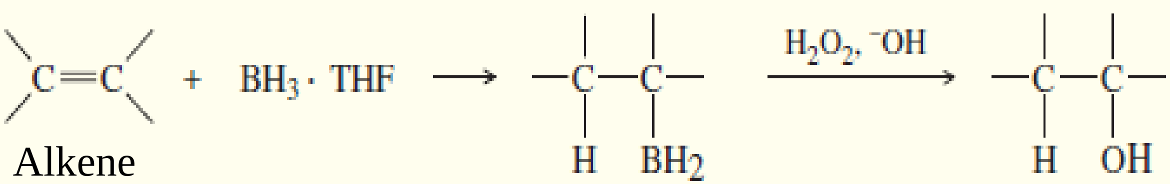
(Markovnikov orientation)

Example

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

propene → propan-2-ol

3-Hydroboration–oxidation:



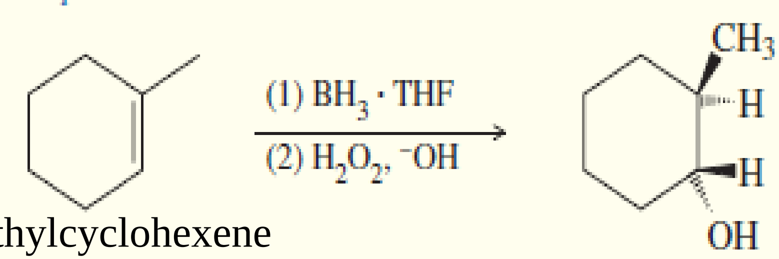
Alkene

1-Hydroborationaklane

Alcohol

anti-Markovnikov orientation (syn addition)

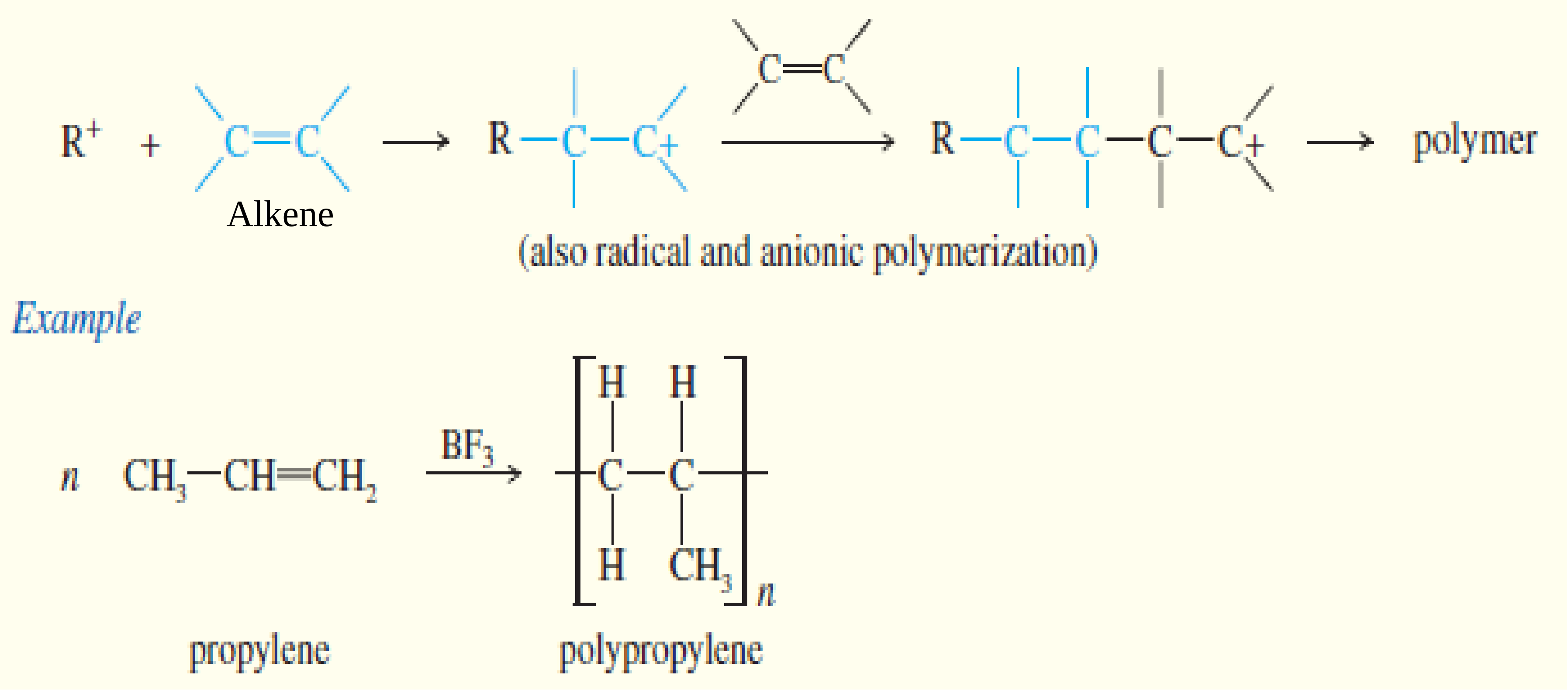
Example



1-methylcyclohexene → 2-methylcyclohexanol

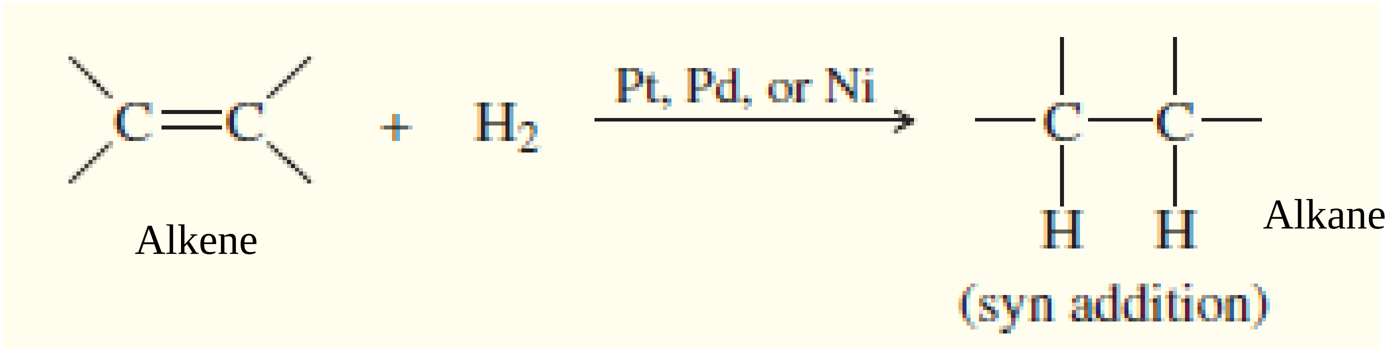
Reaction of Alkenes

4- Polymerization:

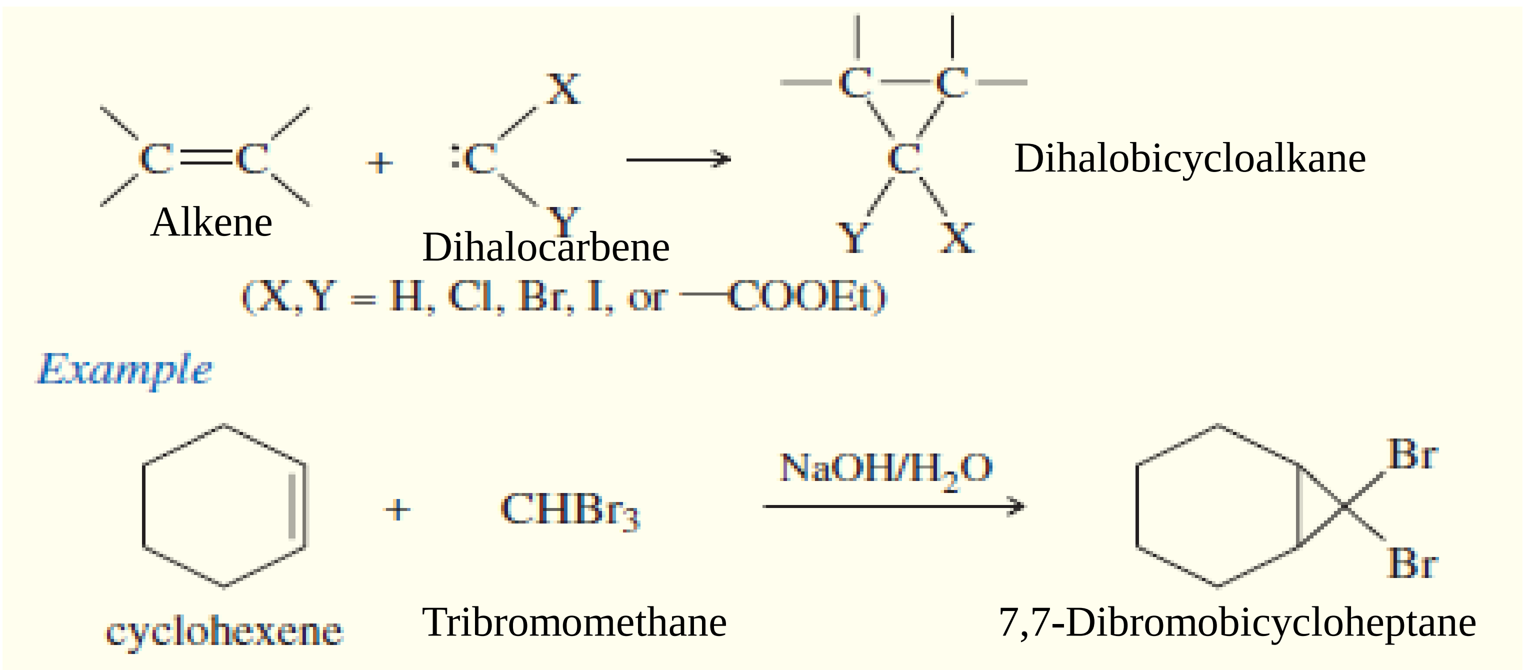


Reaction of Alkenes

5- Reduction: catalytic hydrogenation:

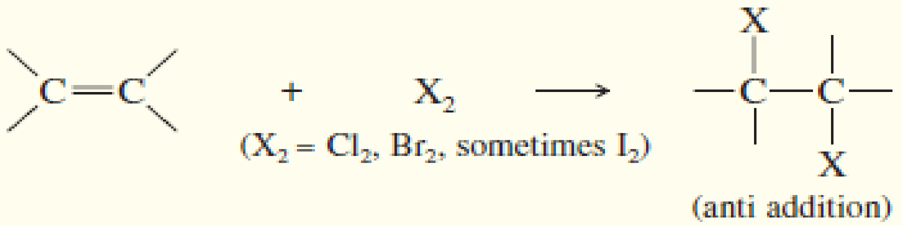


6- Addition of carbenes: cyclopropanation:

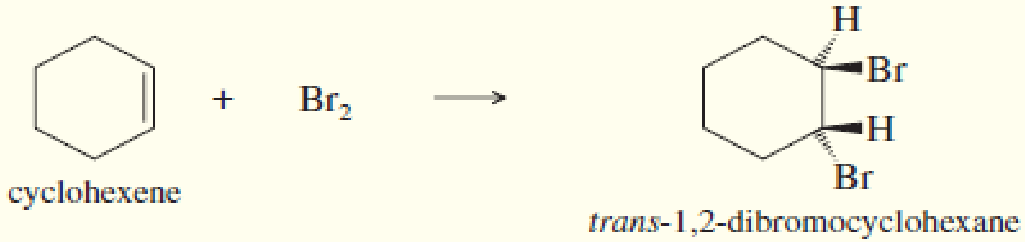


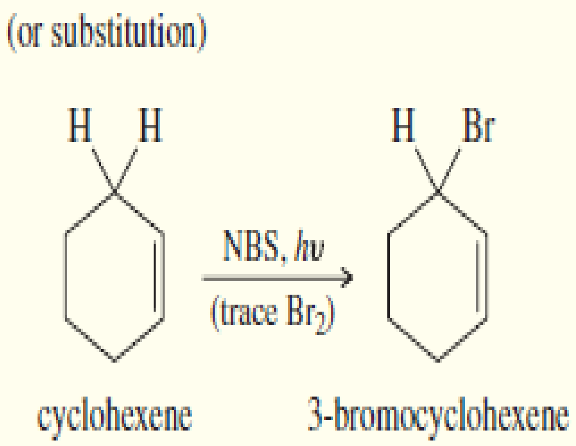
Reaction of Alkenes

7- Addition of halogens:



Example

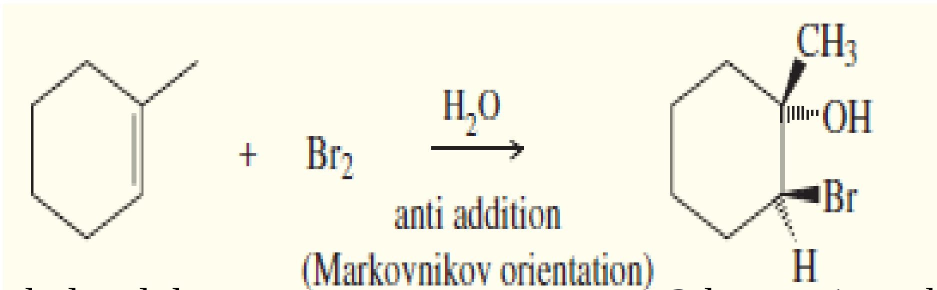




At low concentrations of Br_2, an allylic substitution may be observed. NBS provides a trace of Br_2 that (with light as initiator) allows radical substitution to proceed faster than the ionic addition. (Section 6-6B)

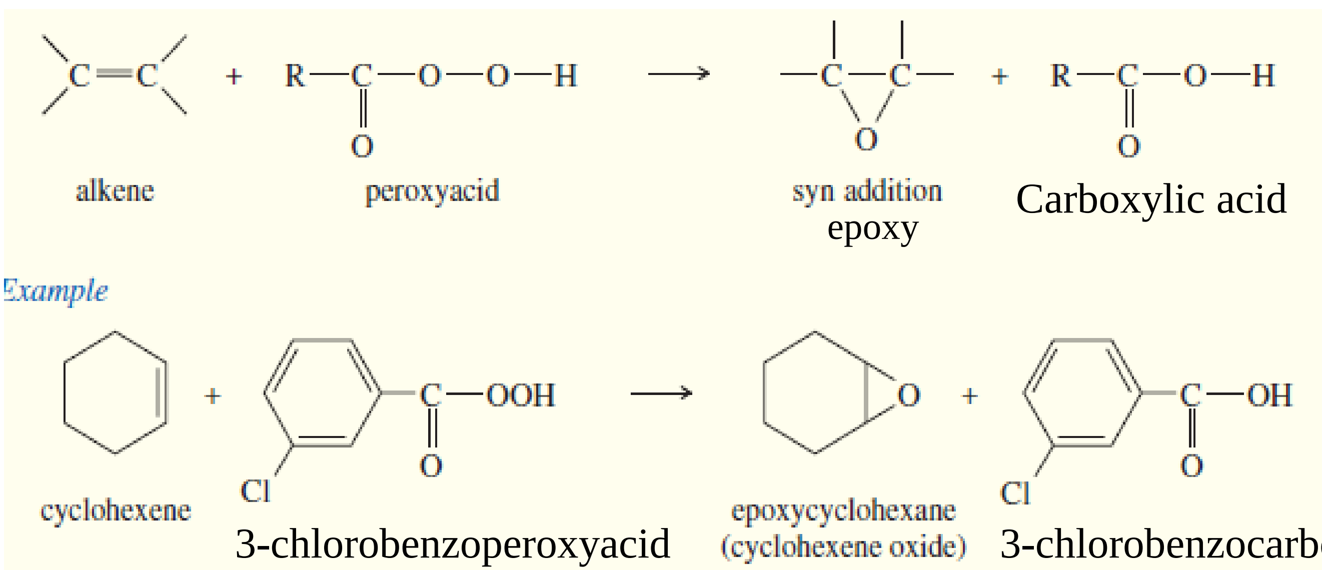
Reaction of Alkenes

8-Halohydrin formation:



1-methylcyclohexene 2-bromo,1-methylcyclohexanol

9- Epoxidation:



epoxy

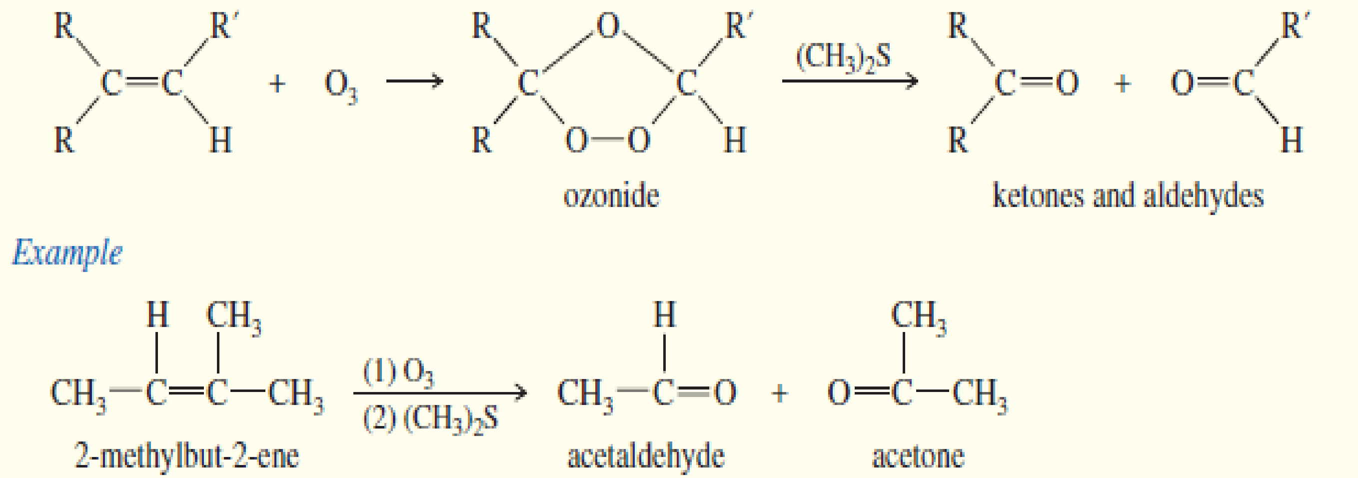
Carboxylic acid

3-chlorobenzoperoxyacid

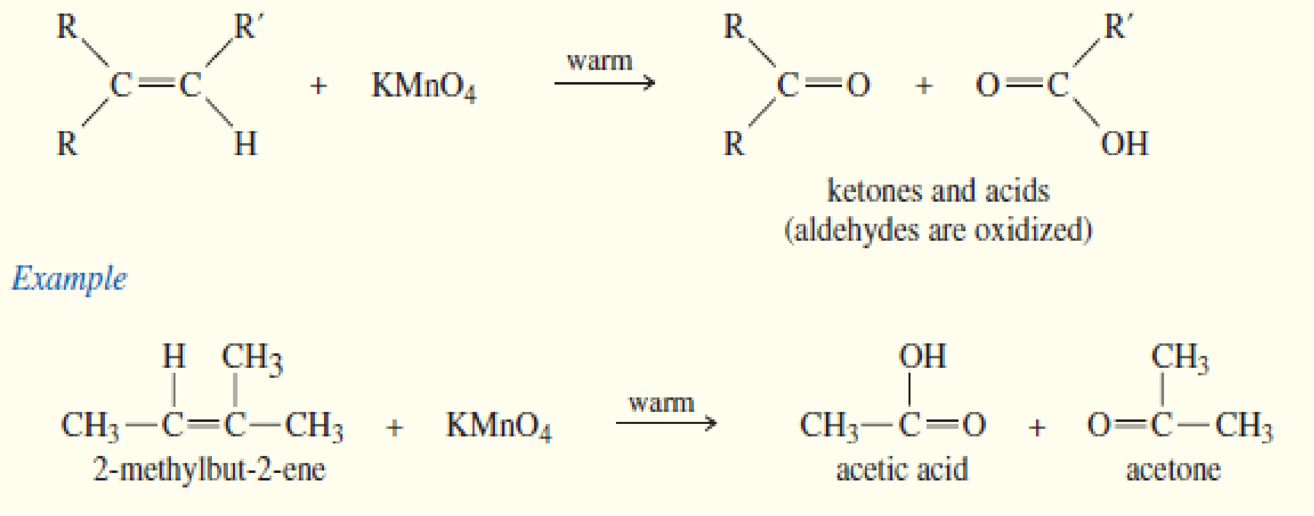
3-chlorobenzocarboxylicacid

Reaction of Alkenes

10- Ozonolysis:



11- Potassium permanganate:



Alkynes

Aliphatics

Unsaturated hydrocarbons: Alkynes

- Unsaturated hydrocarbons (Alkynes):

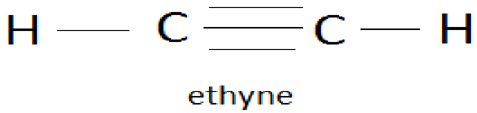
1- They are hydrocarbons contain fewer hydrogens than do alkanes having the same number of carbon atoms.

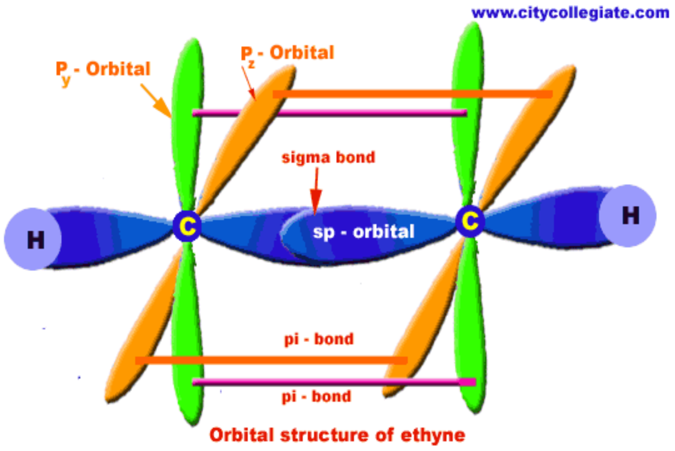
2-These compounds are deficient in hydrogen that why called unsaturated.

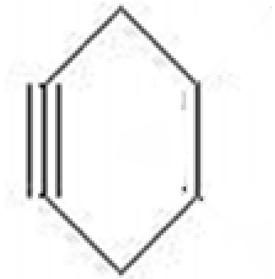
3- Characterized by: the presence of a carbon-carbon triple bonds is called the alkynes and has the general formula C_nH_{2n-2}.

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

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

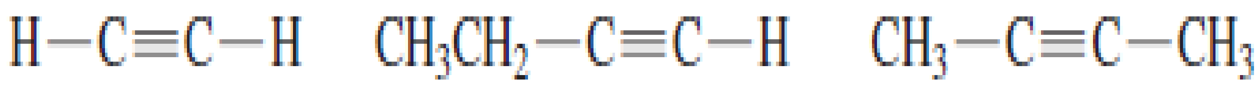






Alkynes

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



acetylene	ethylacetylene	dimethylacetylene
ethyne	but-1-yne	but-2-yne

Physical Properties of Alkynes

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

1- Solubility:

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

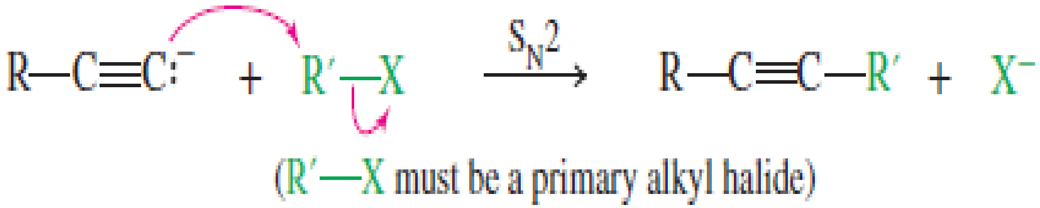
2- Boiling point:

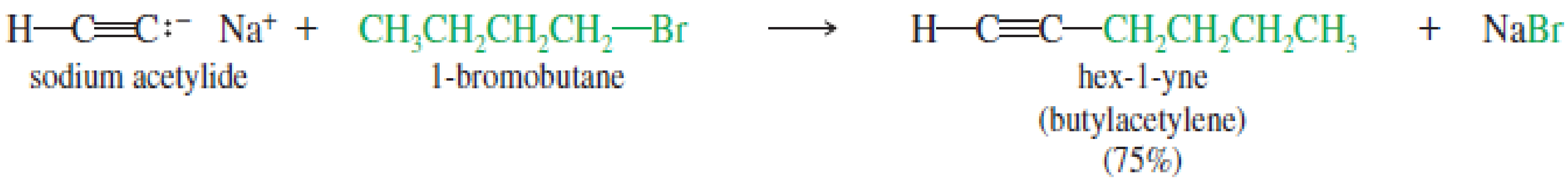
It is increasing with increasing molecular weight. In fact, the boiling points of alkynes are nearly the same as those of alkanes and alkenes with similar carbon skeletons.

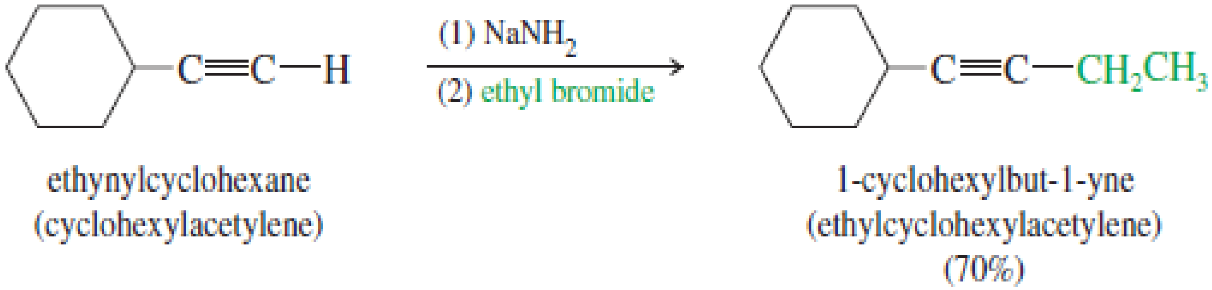
Preparation of Alkynes

1. Alkylation of acetylide ions:

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



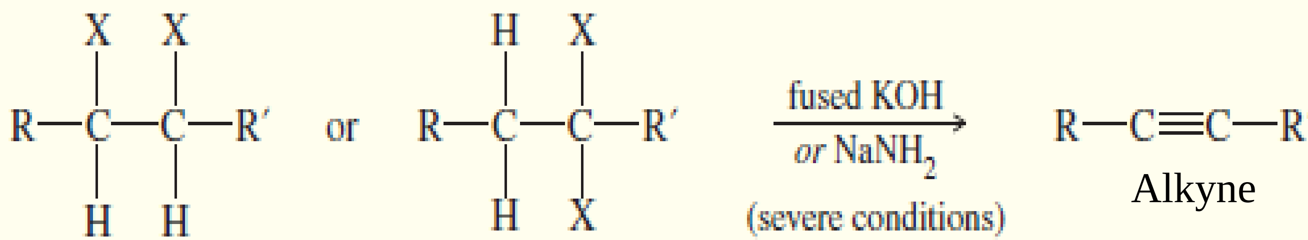




Preparation of Alkynes

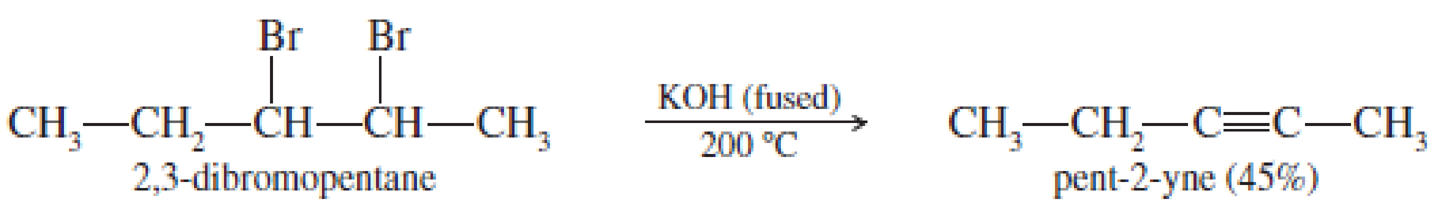
2- Double dehydrohalogenation of alkyl dihalides:

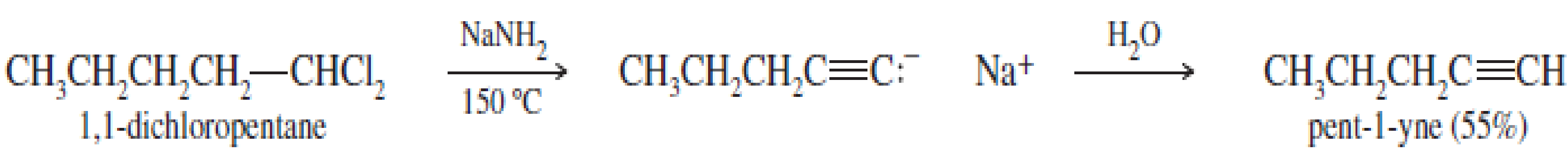
In some cases, we can generate a carbon–carbon triple bond by eliminating two molecules of HX from a dihalide. Dehydrohalogenation of a geminal or vicinal dihalide gives a vinyl halide. Under strongly basic conditions, a second dehydrohalogenation may occur to form an alkyne.



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

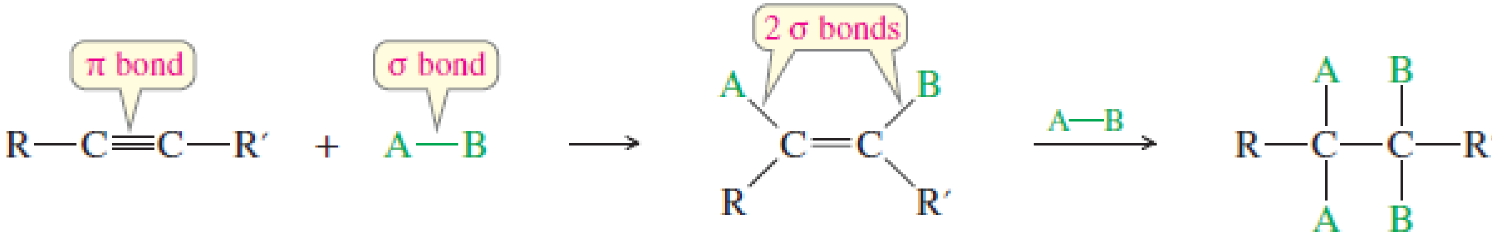
Example:





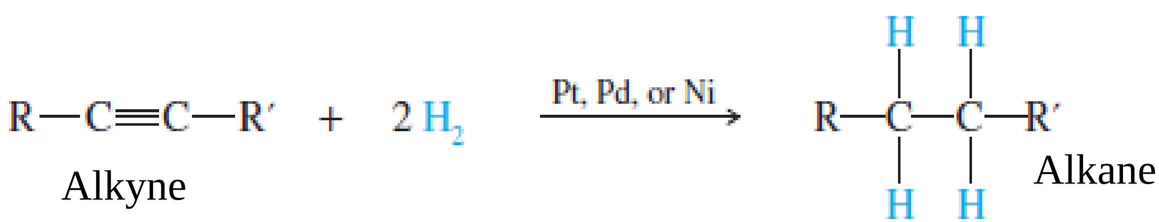
Reaction of alkynes

1-Addition reactions of alkynes:



a-Catalytic hydrogenation to alkanes:

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



Examples:

$$H-C\equiv C-CH_2CH_3 + 2\,H_2 \xrightarrow{Pt} H-CH_2-CH_2-CH_2CH_3$$

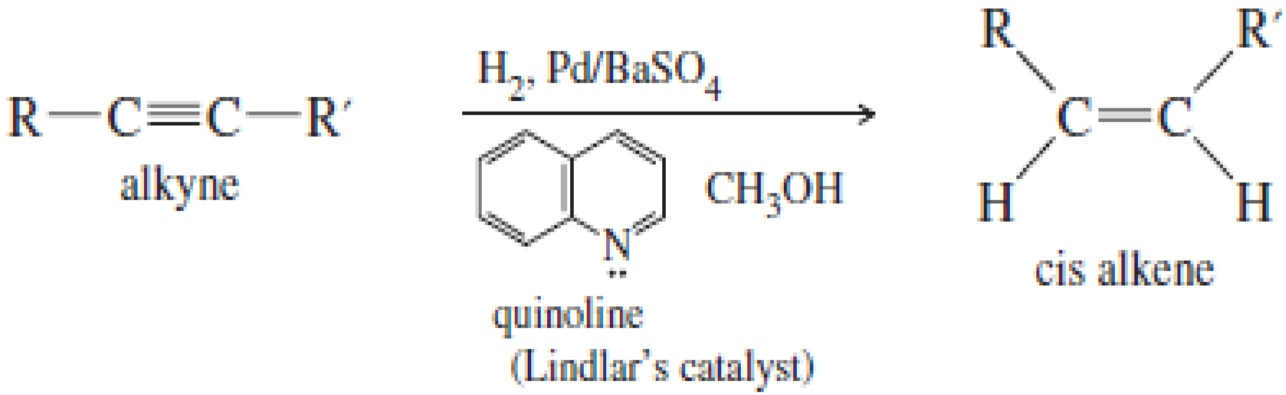
but-1-yne → butane (100%)

$$CH_3-C\equiv C-CH_3 + 2\,H_2 \xrightarrow{Pt} CH_3-CH_2-CH_2-CH_3$$

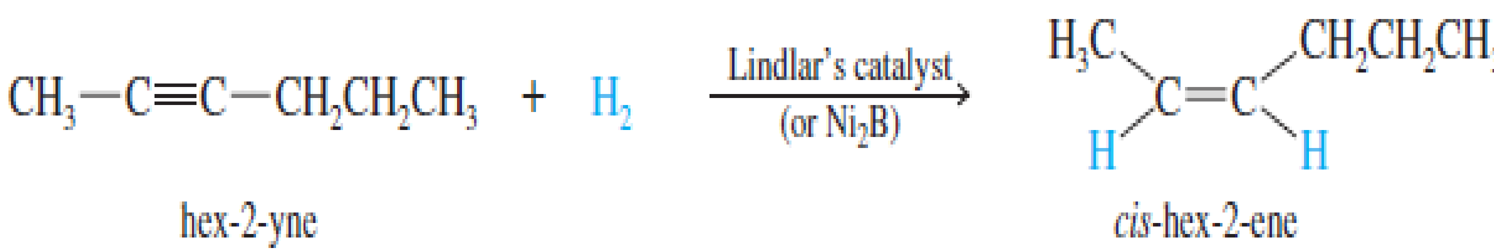
but-2-yne → butane (100%)

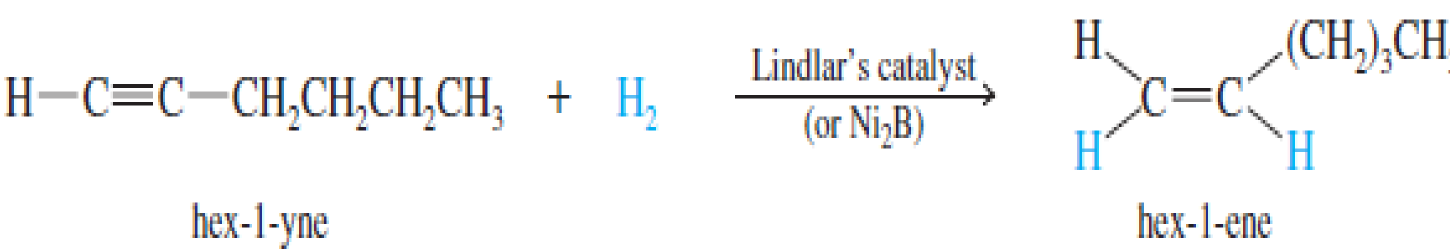
Reaction of alkynes

b- Catalytic hydrogenation to cis alkenes:



Example:

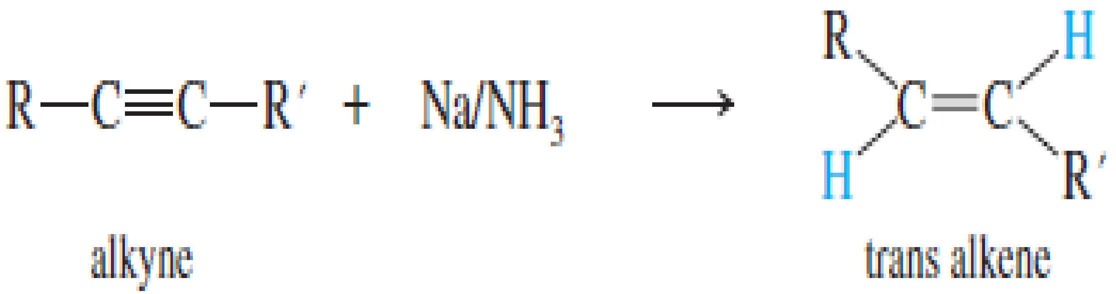




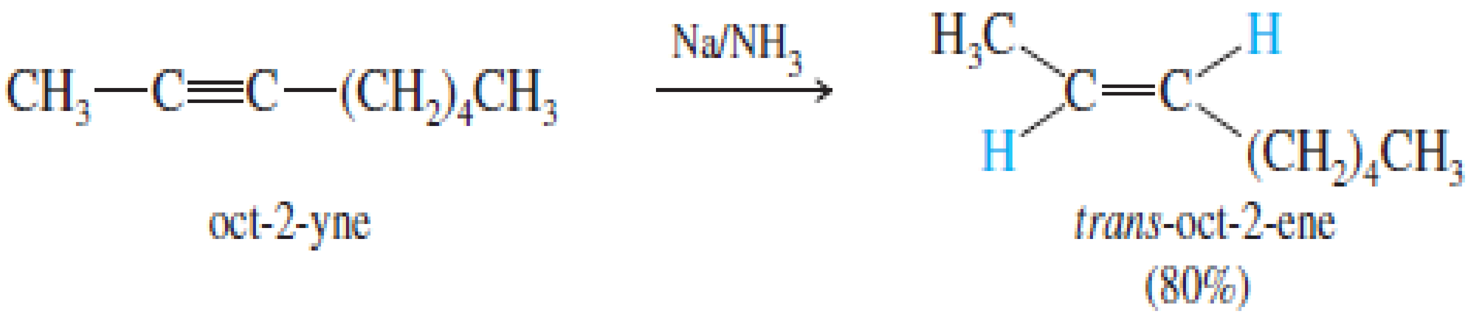
Reaction of alkynes

c-Metal–ammonia reduction to trans alkenes:

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



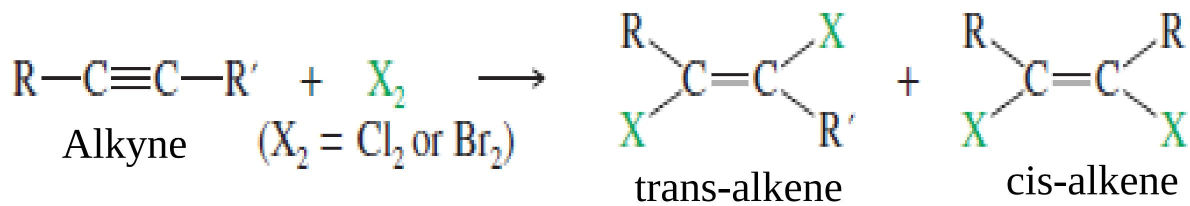
Example:



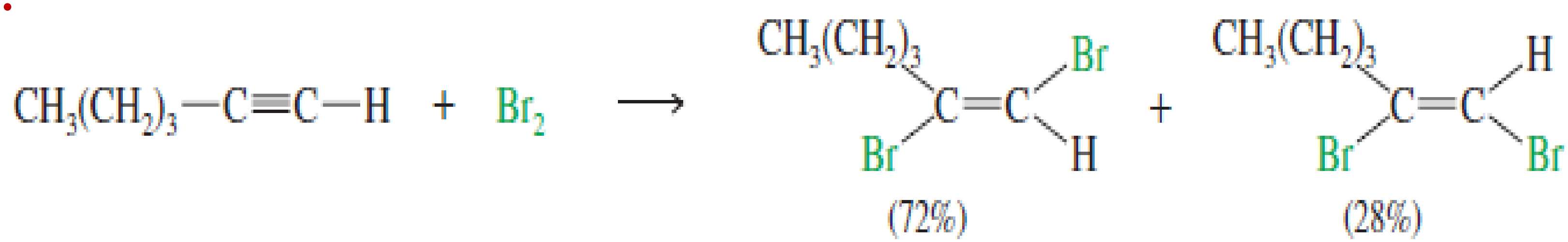
Reaction of alkynes

2- Addition of Halogens:

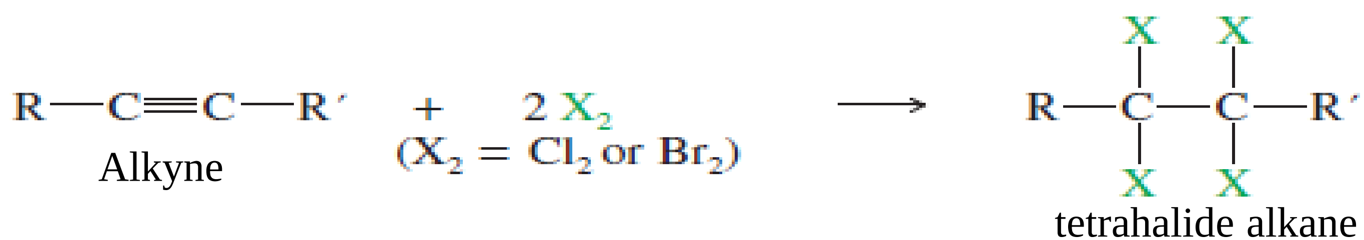
Bromine and chlorine add to alkynes just as they add to alkenes. If 1 mole of halogen adds to 1 mole of an alkyne, the product is a dihaloalkene. The stereochemistry of addition may be either syn or anti, and the products are often mixtures of cis and trans isomers.



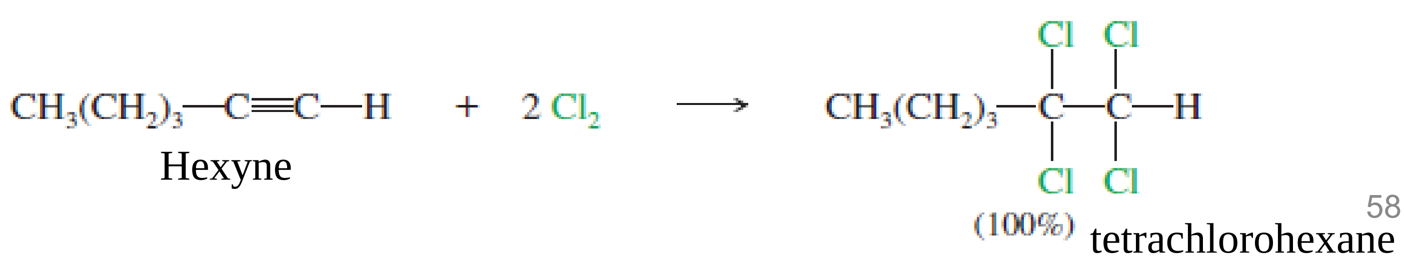
Example:



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



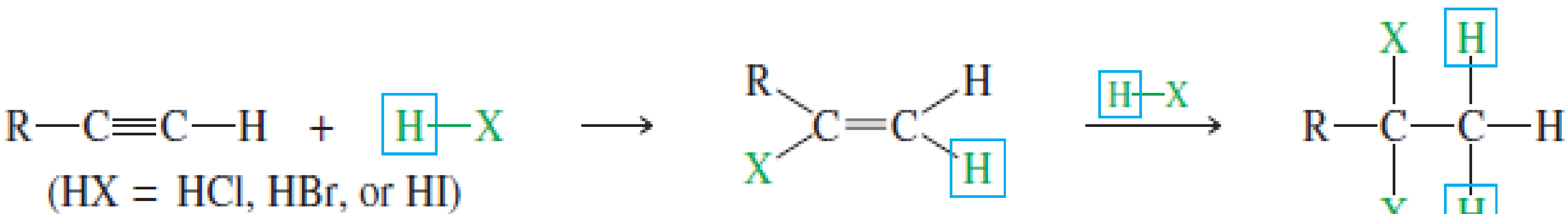
Example:



Reaction of alkynes

3- Addition of hydrogen halides:

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

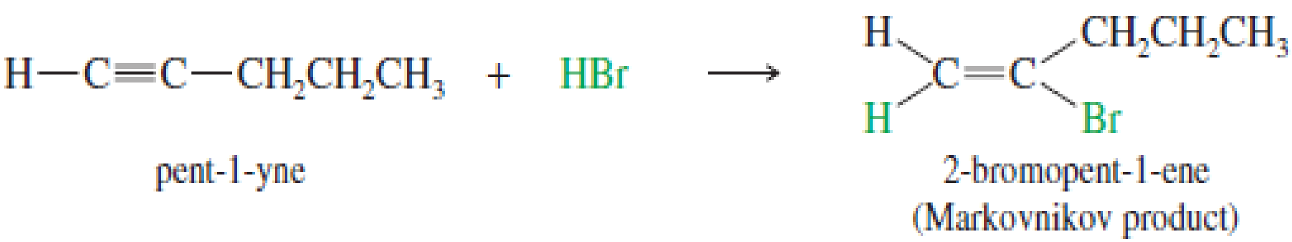


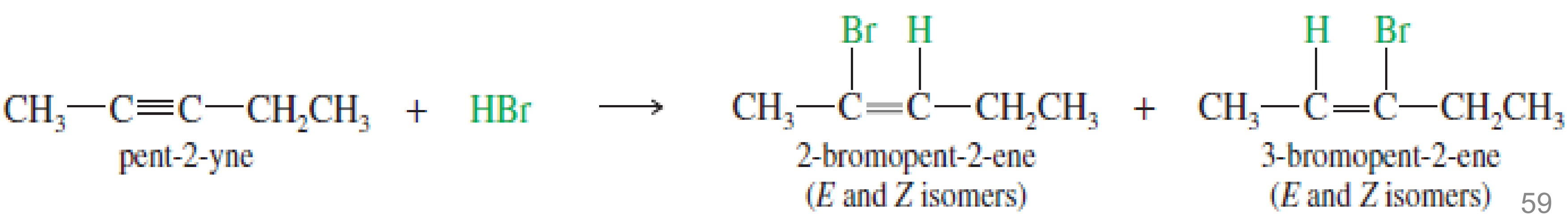
Alkyne

Halide alkene

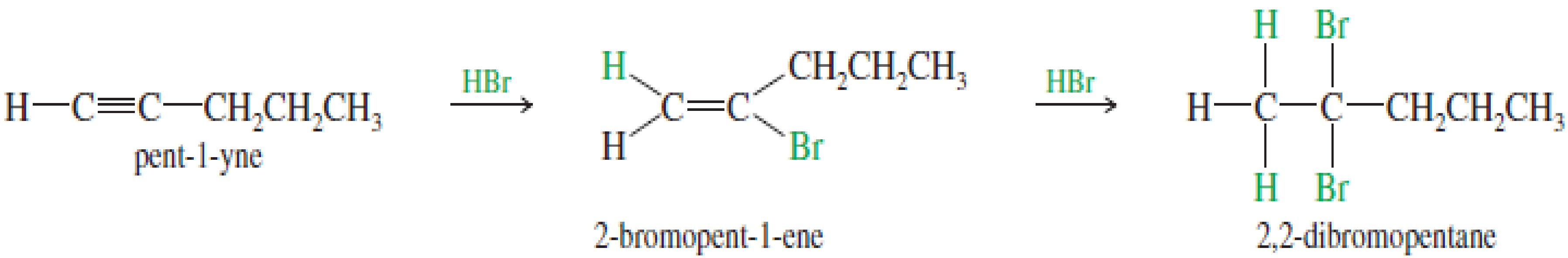
Dihalide alkane

Example:

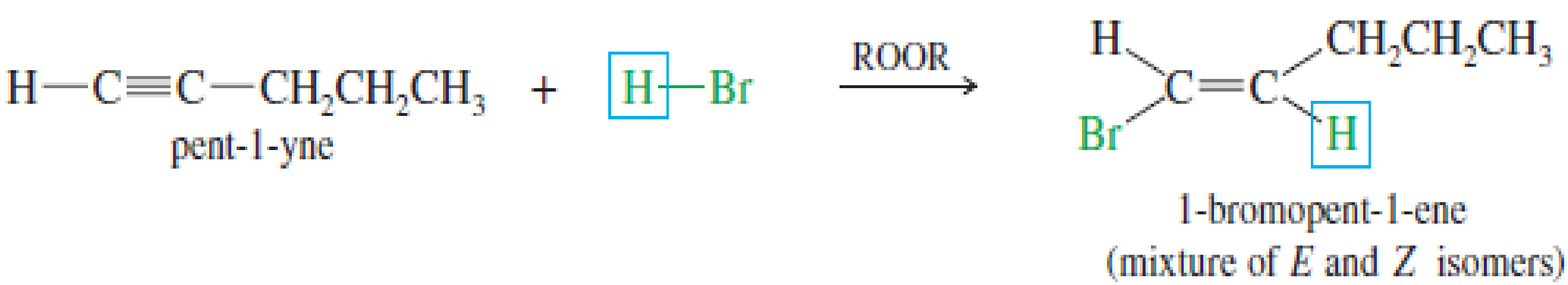




Reaction of alkynes



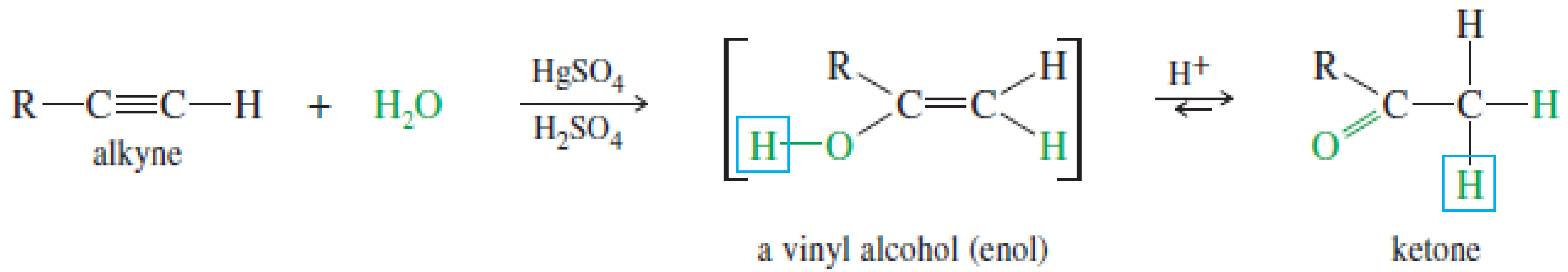
Peroxides catalyze a free-radical chain reaction that adds HBr across the double bond of an alkene in the anti-Markovnikov sense. A similar reaction occurs with alkynes, with HBr adding with anti-Markovnikov orientation.



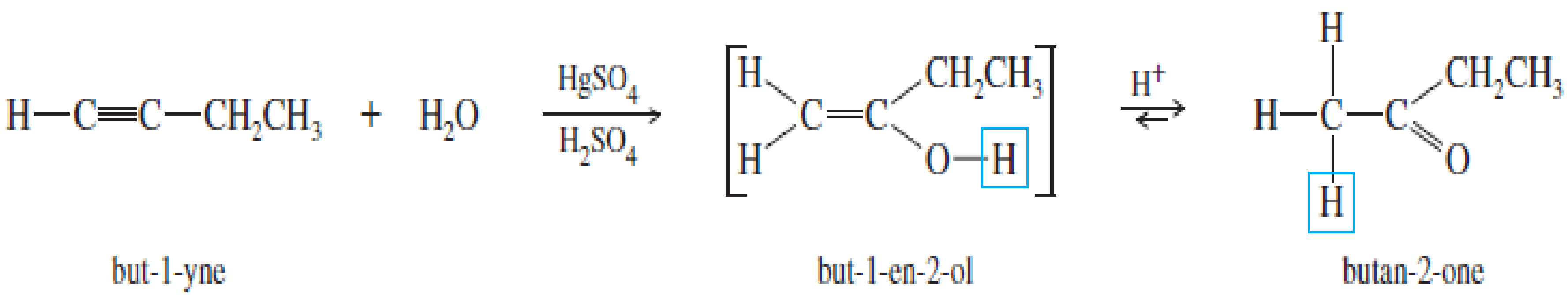
Reaction of alkynes

4- Hydration of alkynes to ketones and aldehydes:

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



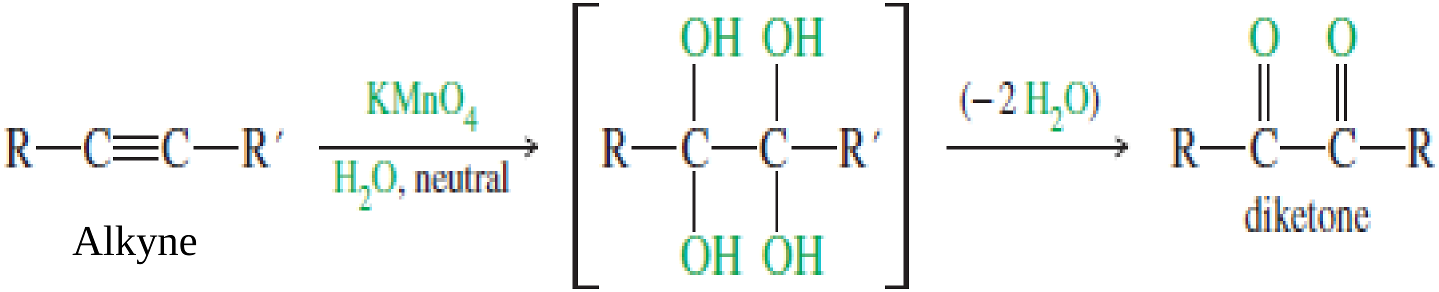
For example, the mercuric-catalyzed hydration of but-1-yne gives but-1-en-2-ol as an intermediate. In the acidic solution, the intermediate quickly equilibrates to its more stable keto tautomer, butan-2-one.



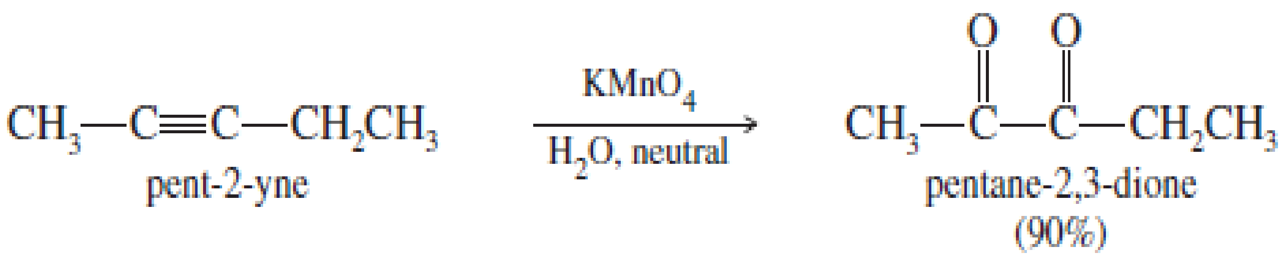
Reaction of alkynes

5- Oxidation of alkynes

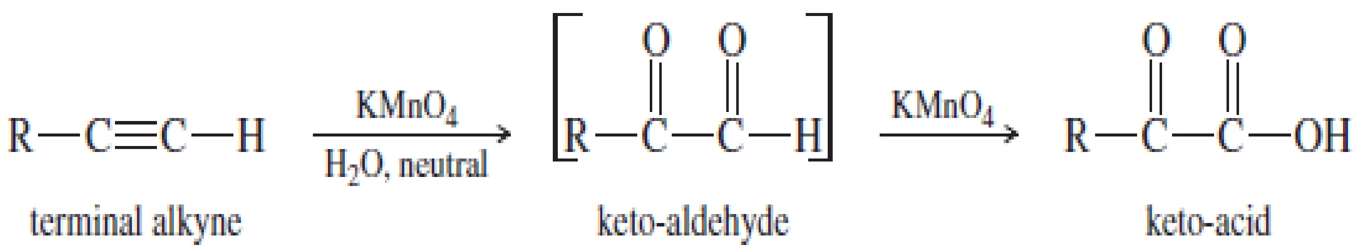
a- Permanganate oxidations:



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



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

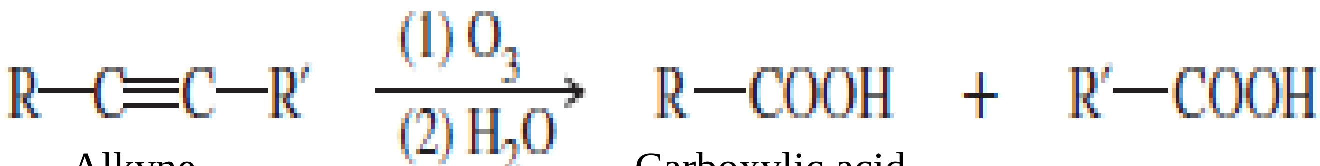


Reaction of alkynes

b-Ozonolysis:

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

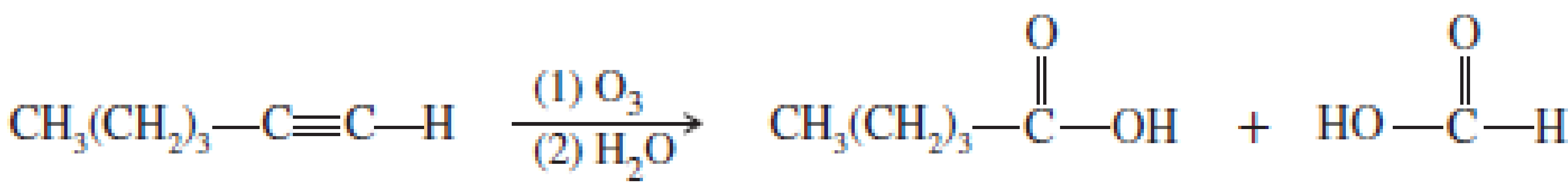
Ozone



Alkyne Carboxylic acid

Examples:

pent-2-yne acetic acid propionic acid



hex-1-yne pentanoic acid formic acid

Aromatics hydrocarbons

Aromatics hydrocarbons

- **Aromatics hydrocarbons:**

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

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

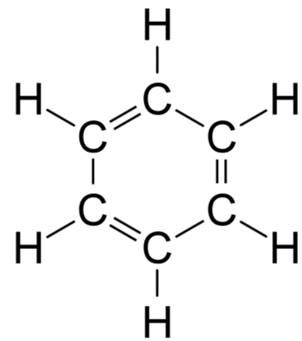
3- Substances that contained the C_6H_6 unit are with odorless and vile-smelling.

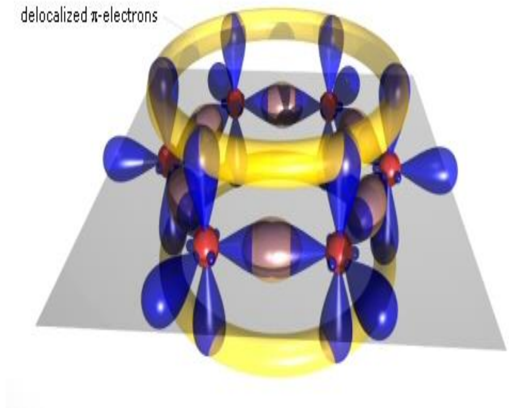
4-They are unsaturated hydrocarbons.

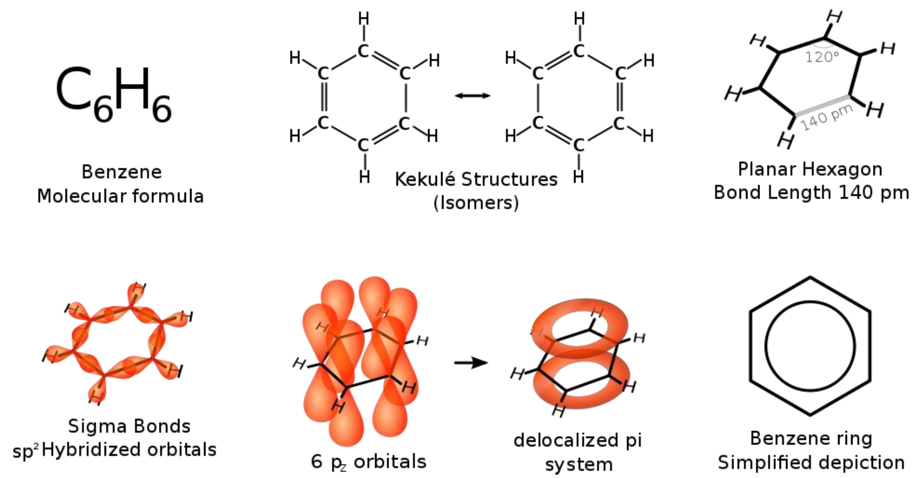
5-Characterized by alternate double bonds.

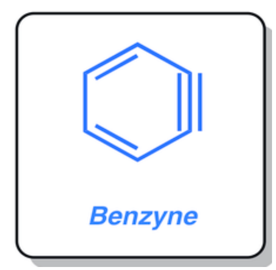
6-Their physical and chemical characteristics are different than aliphatics.

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







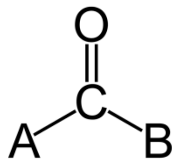


Aldehydes and Ketones

Carbonyl compounds

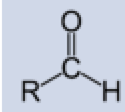
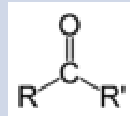
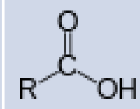
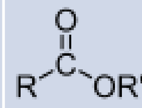
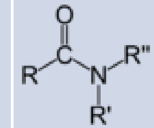
- **Definition of carbonyl compounds:**

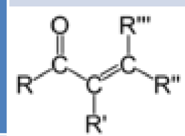
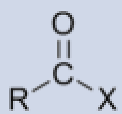
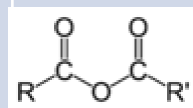
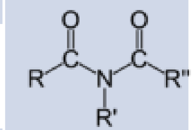
1. They are an organic compounds that contain the carbonyl group, which consists of a carbon-oxygen double bond.



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

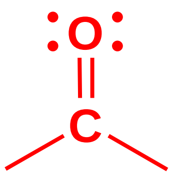
3. A carbonyl group characterizes the following types of compounds:

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

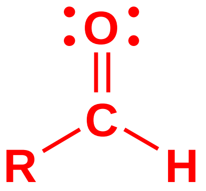
Compound	Enone	Acyl halide	Acid anhydride	Imide
Structure				
General formula	RC(O)C(R')CR''R'''	RCOX	$(RCO)_2O$	RC(O)N(R')C(O)R''

Aldehydes and Ketones

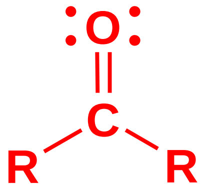
1. **Aldehydes** are organic compounds that carbonyl carbon of the carbonyl group is bonded to hydrogen, with general formula **RCHO.**
2. **Ketones** are organic compounds that carbonyl carbon of the carbonyl group is bonded to carbon, with general formula **RCOR´.**
3. The groups R and R´ may be aliphatic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



Carbonyl group



Aldehyde

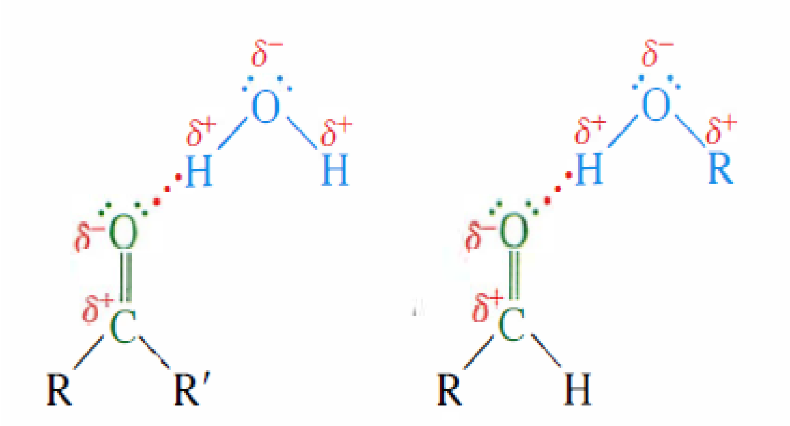


Ketone

Physical Properties of Aldehydes and Ketones

- **Solubility:**

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



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

- **Boiling point**:

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

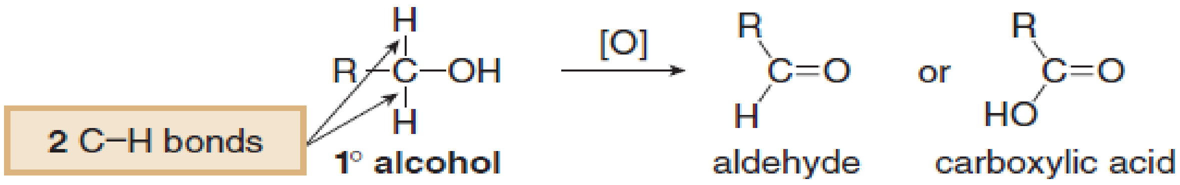
➢ They have **lower boiling points** than comparable **alcohols or carboxylic acids** due to the **intermolecular hydrogen bonding**.

Preparation of aldehydes & Ketones

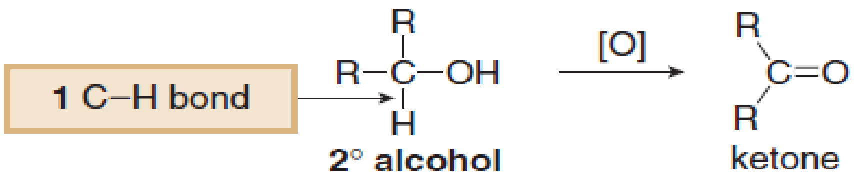
Introduction:

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

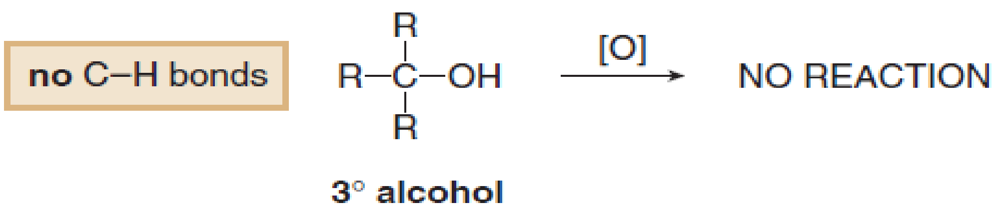
- 1° **Alcohols** are oxidized to either **aldehydes** or **carboxylic acids** by replacing either one or two C–H bonds by C–O bonds.



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



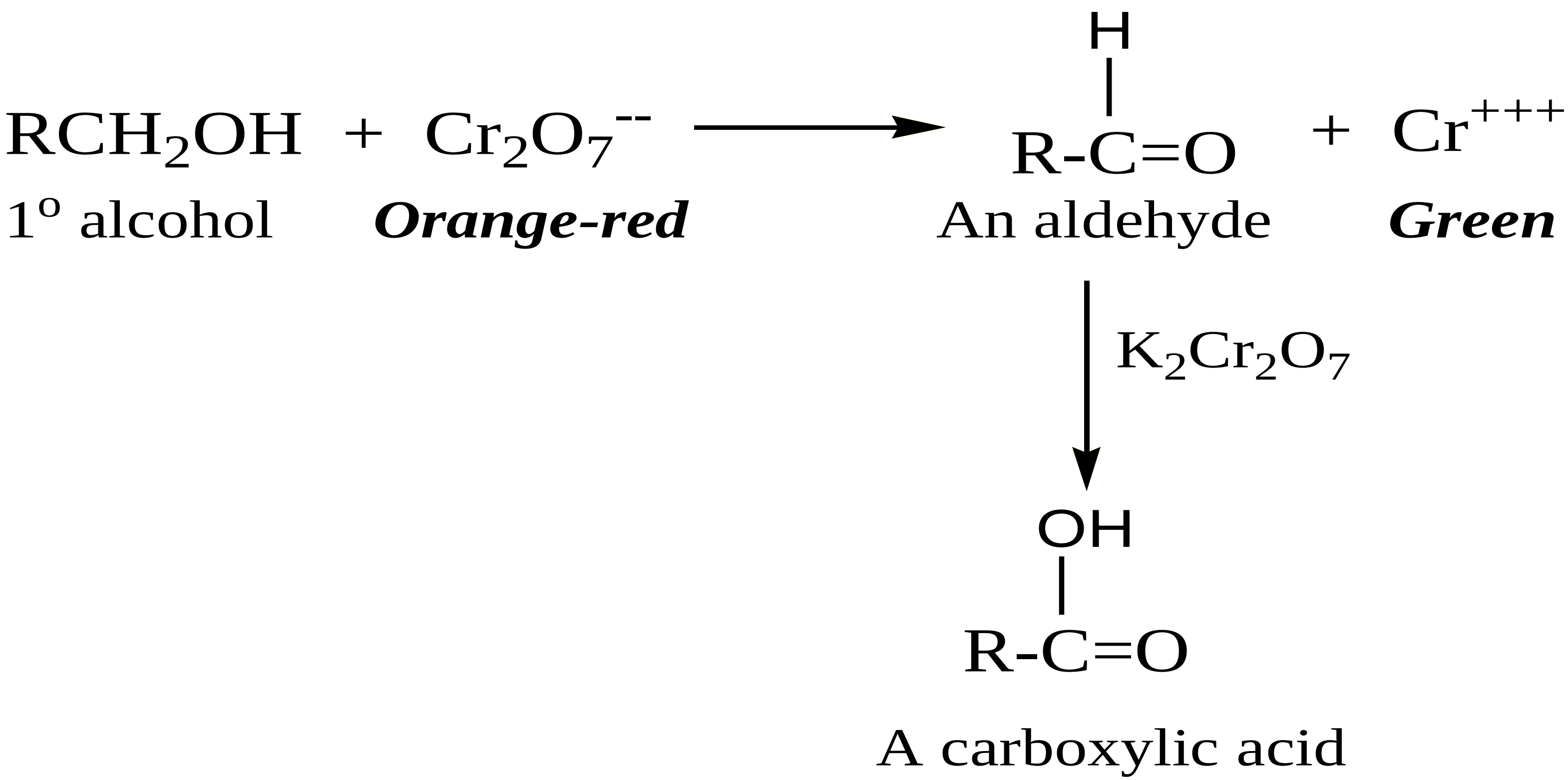
- 3° **Alcohols have no H atoms on the carbon with the OH group,** so they are not easily oxidized.



Preparation of aldehydes

1- Oxidation of primary alcohols:

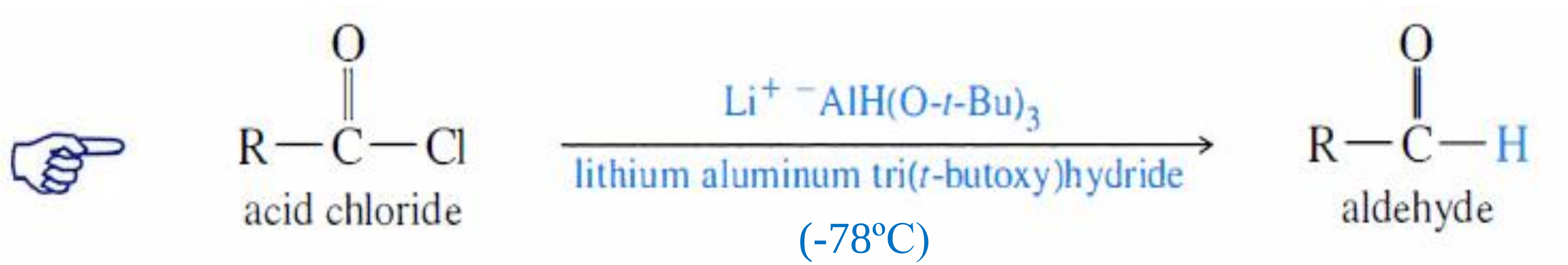
[O] can be hot copper Cu or chromium oxide CrO_3 in pyridine (mild oxidizing agent) or by dichromic acid $H_2Cr_2O_7$ or potassium dichromic acid $K_2Cr_2O_7$.



Preparation of aldehydes

2. Partial reduction of acid chlorides:

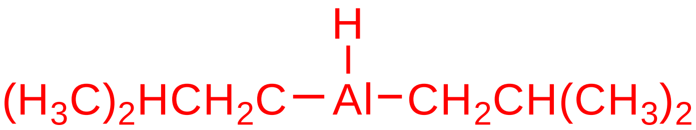
- **Strong reducing agents** (like **$LiAlH_4$**) reduce **acid chlorides** all the way to **primary alcohols**.
- **Lithium aluminum tri(*t*-butoxy)hydride** is a **milder reducing agent** that reacts faster with acid chlorides than with aldehydes. Reduction of **acid chlorides** with lithium aluminum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



(-78ºC)

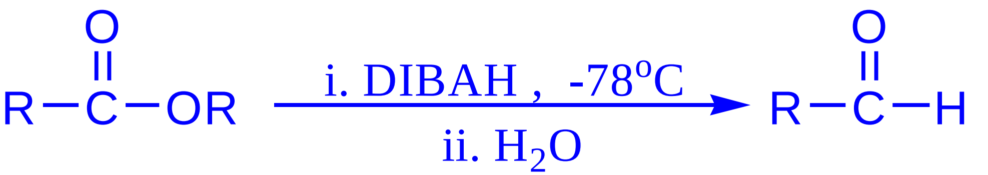
Preparation of aldehydes

Diisobutylaluminium hydride
(*mild reducing agent*)



3. Partial reduction of esters:

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



Ester **Aldehyde**

4. Reduction of Nitriles:

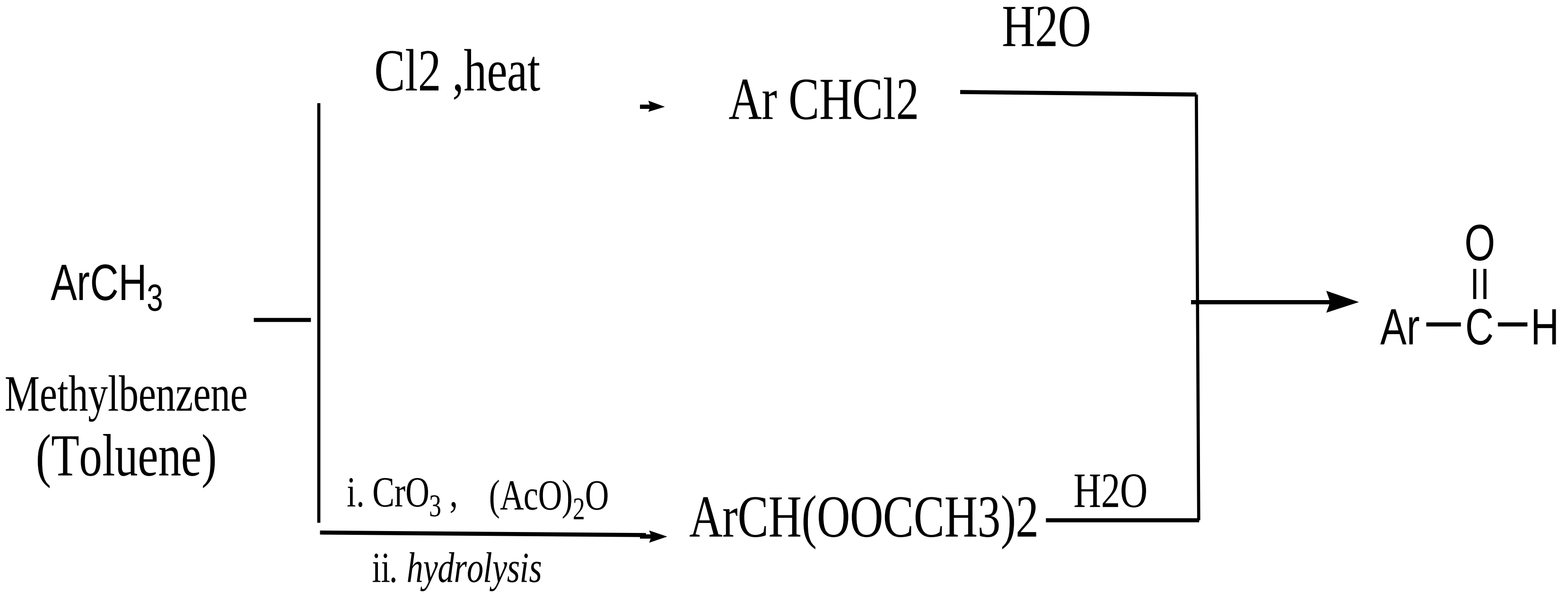
Reduction of nitrile with a less powerful reducing reagent, e.g. **DIBAH**, produces aldehyde. The reaction is carried out at low temperatures (-78ºC) in toluene.

Nitrile Aldehyde

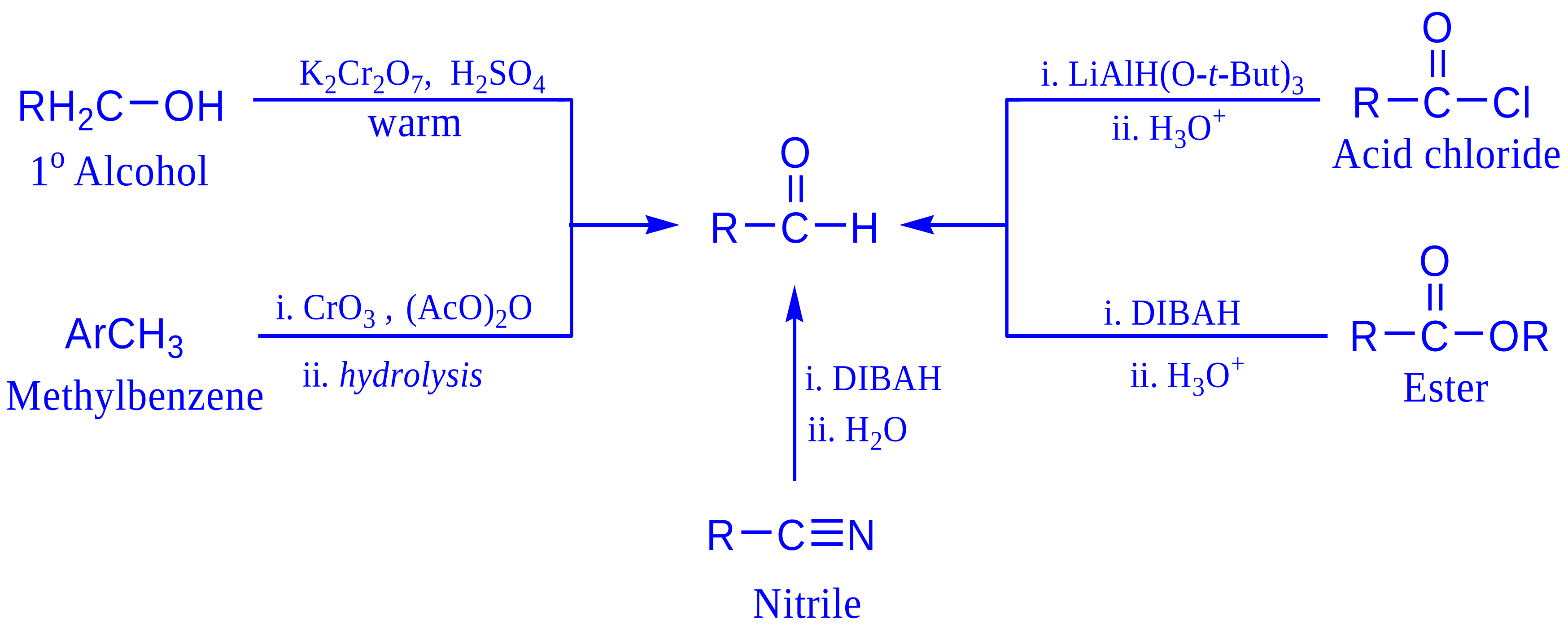
Preparation of aldehydes

5. Oxidation of methylbenzene:

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



Review on preparation of aldehydes

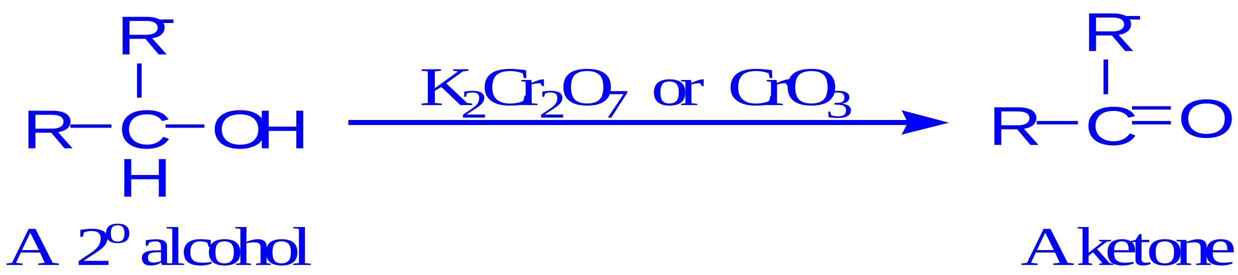


Preparation of ketones

1. Oxidation of Secondary alcohols:

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

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



Preparation of Aldehydes and Ketones

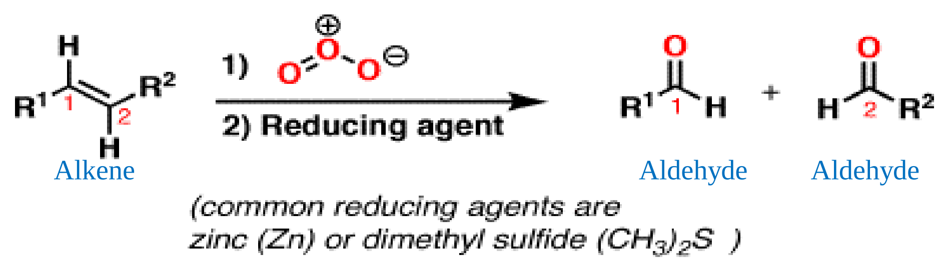
2- Ozonolysis of alkenes:

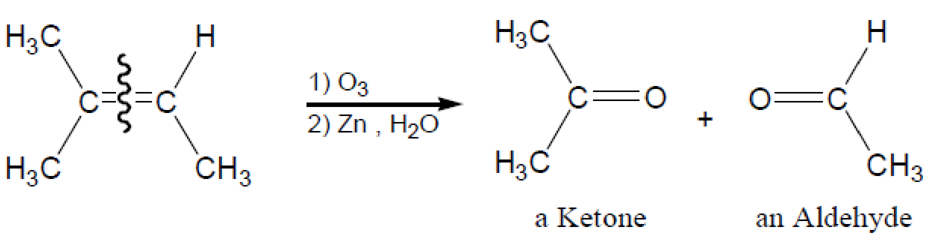
Cleavage of Carbon–Carbon double bond by Ozone:

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

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

Ozonolysis of alkenes with reductive workup



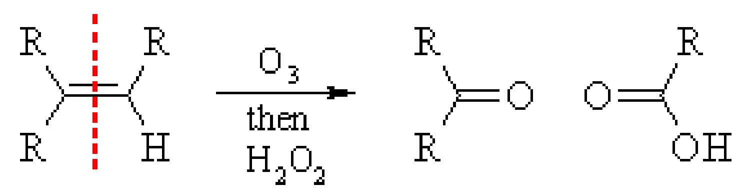


2-Methyl,2-butene

acetone — Dimethyl ketone

acetaldehyde — ethanal

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

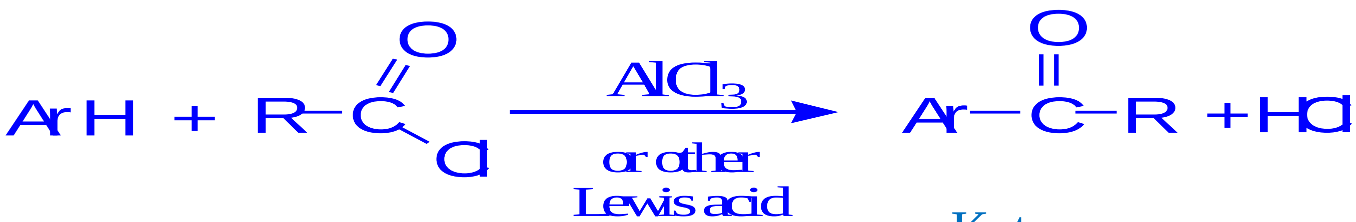


Alkene — Ketone — carboxylic acids

Preparation of Ketones

3. Friedel-Crafts acylation:

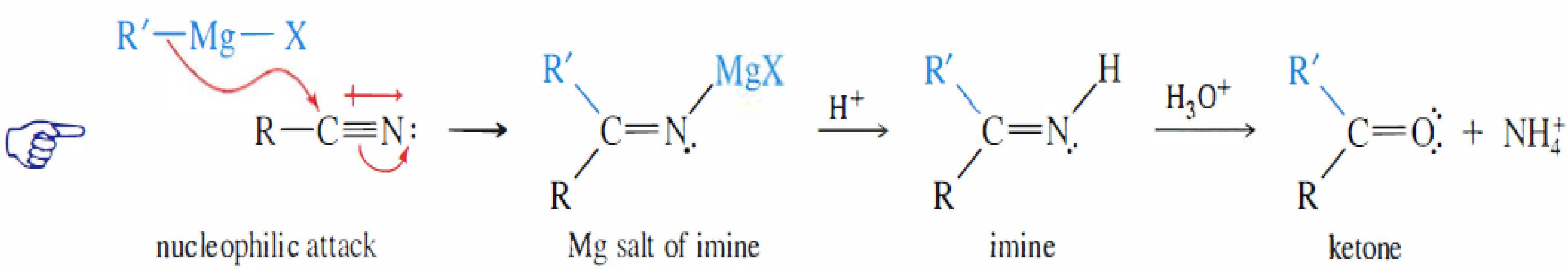
The Friedel-Crafts reaction involves the use of acid chlorides rather than alkyl halides. An acyl group (RCO–) becomes attached to the aromatic ring. Thus forming a ketone; the process is called acylation.



Ketone

4- Synthesis of Ketones from Nitriles:

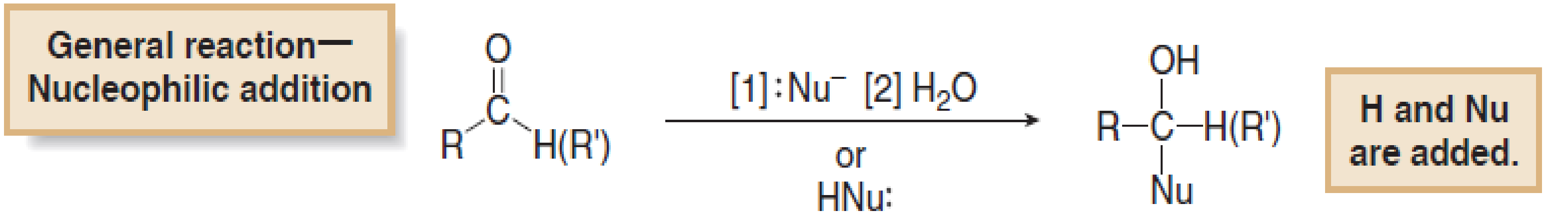
A Grignard or organomagnesium reagent attacks a nitrile to give the magnesium salt of an imine. Acidic hydrolysis of the imine leads to the ketone.



Reaction of Aldehydes and Ketones

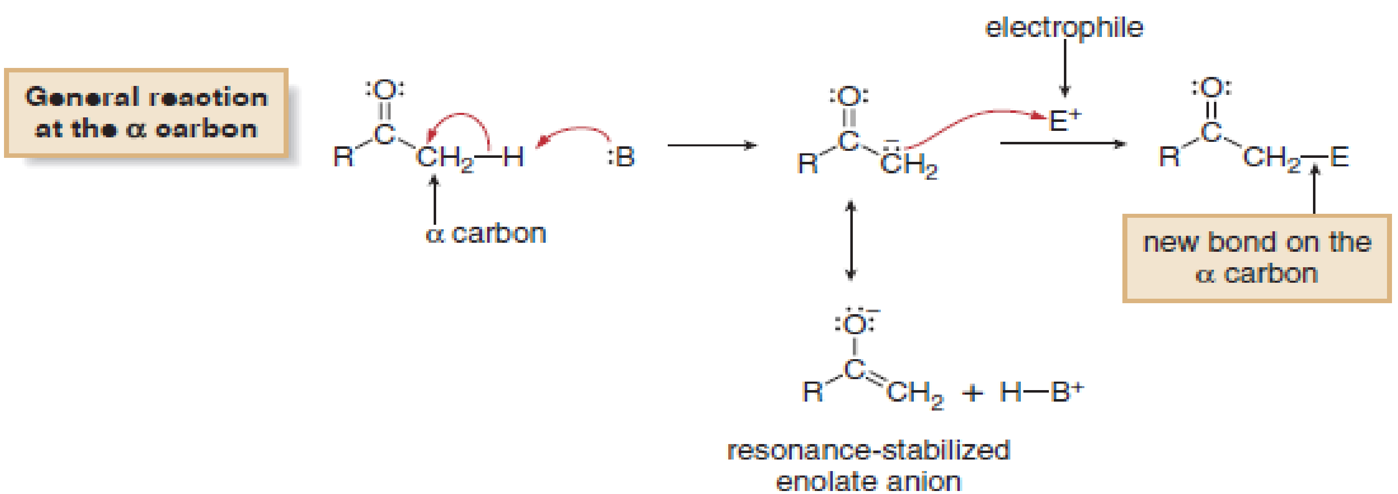
Aldehydes and Ketones undergo many reactions to give a wide variety of useful derivatives. There are two general kinds of reactions that aldehydes and ketones undergo:

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



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

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

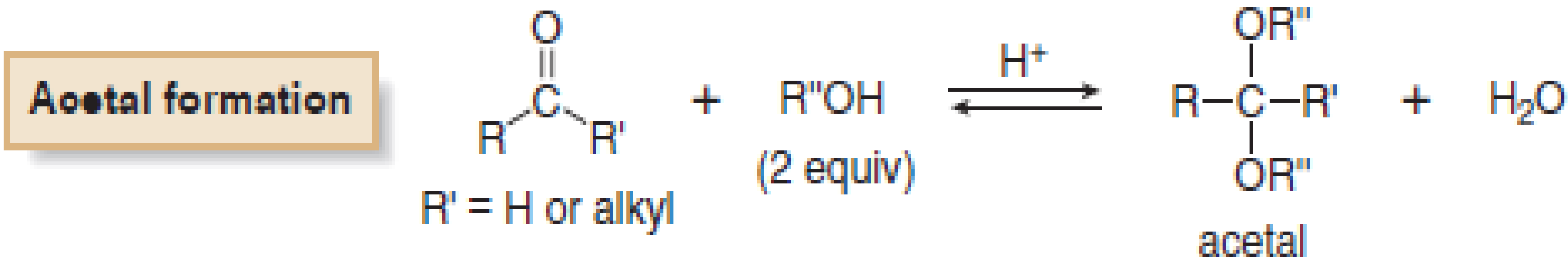


Reaction of Aldehydes and Ketones

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

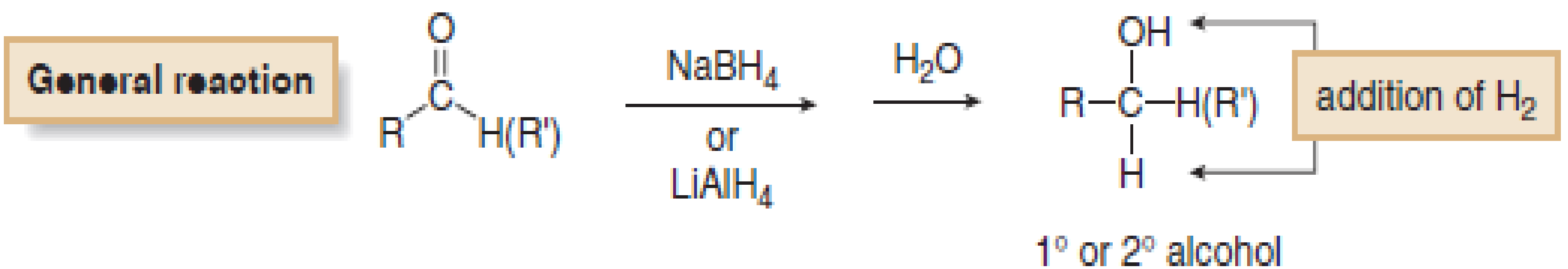
a) Addition of Alcohols (Acetal formation):

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



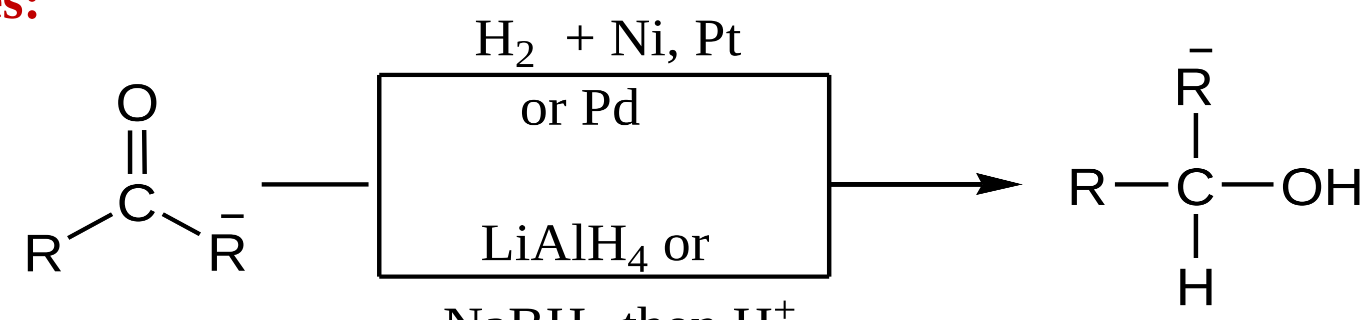
b) Nucleophilic Addition of H_2 (Reduction reaction):

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



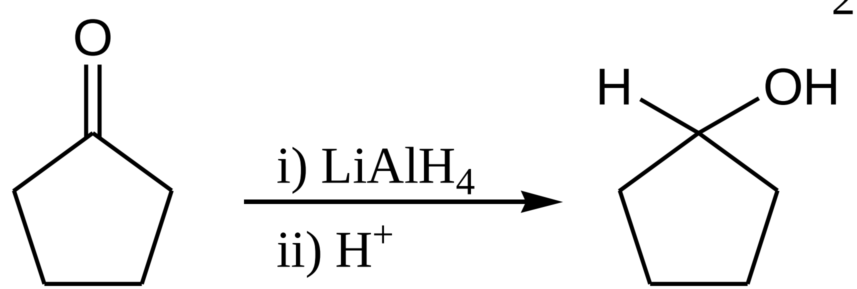
Reaction of Aldehydes and Ketones

Examples:



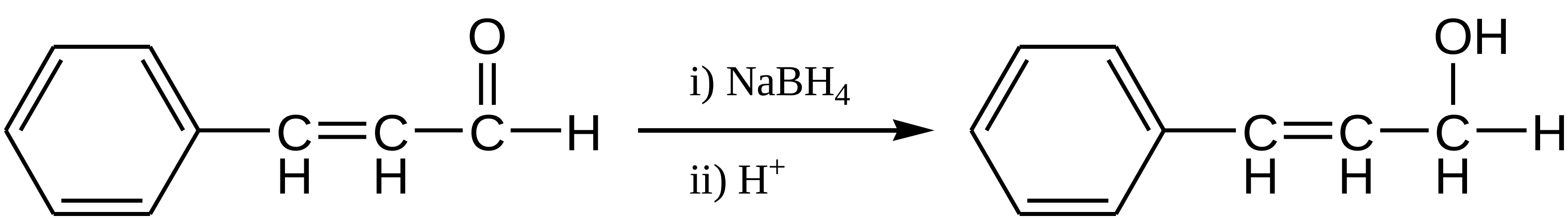
Ketone

2° Alcohol



Cyclopentanone

Cyclopentanol



3-Phenylacrylaldehyde
(Cinnamaldehyde)

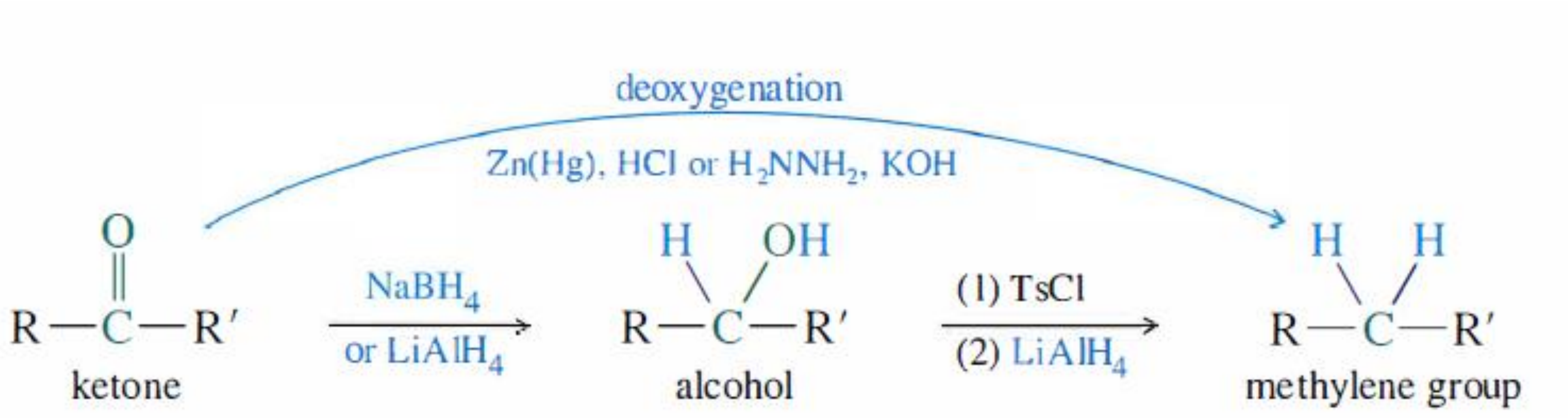
Cinnamyl alcohol

Reaction of Aldehydes and Ketones

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

i) Clemmensen reduction.

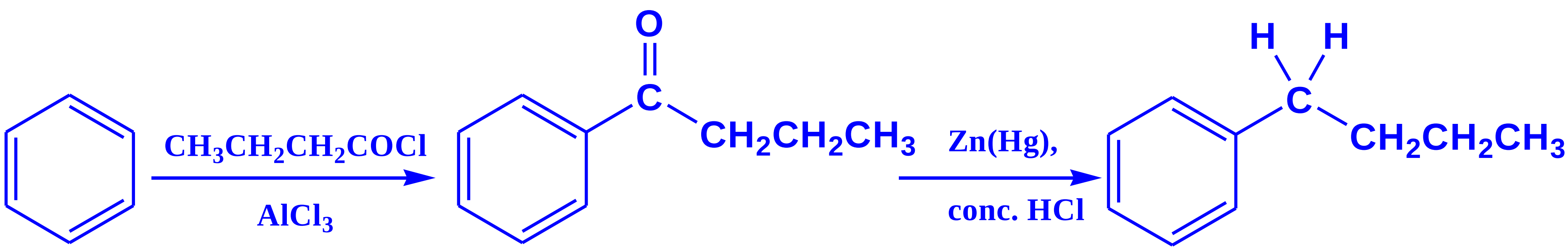
ii) Wolff–Kishner reduction.



Reaction of Aldehydes and Ketones

i) Clemmensen reduction:

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

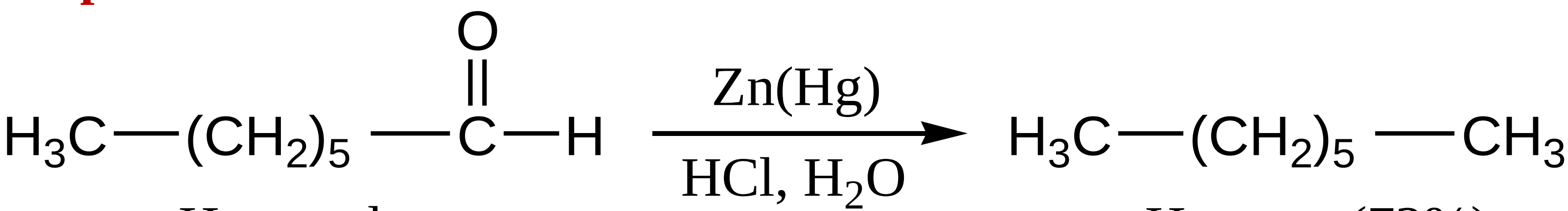


***n*-Butyrophenone** ***n*-Butylbenzene**

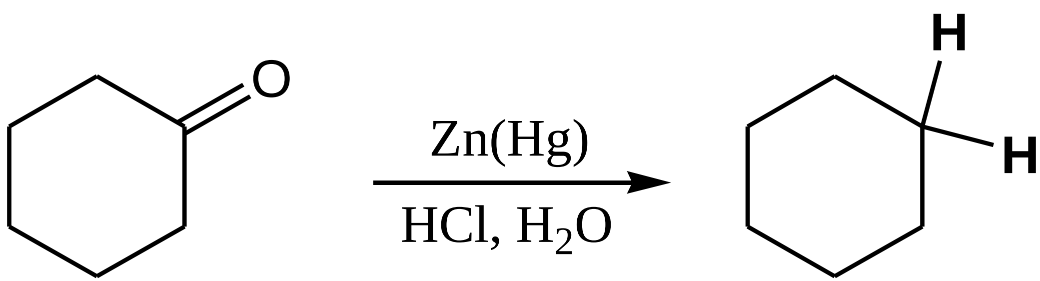
The **Clemmensen reduction** uses zinc and mercury in the presence of strong acid.

Reaction of Aldehydes and Ketones

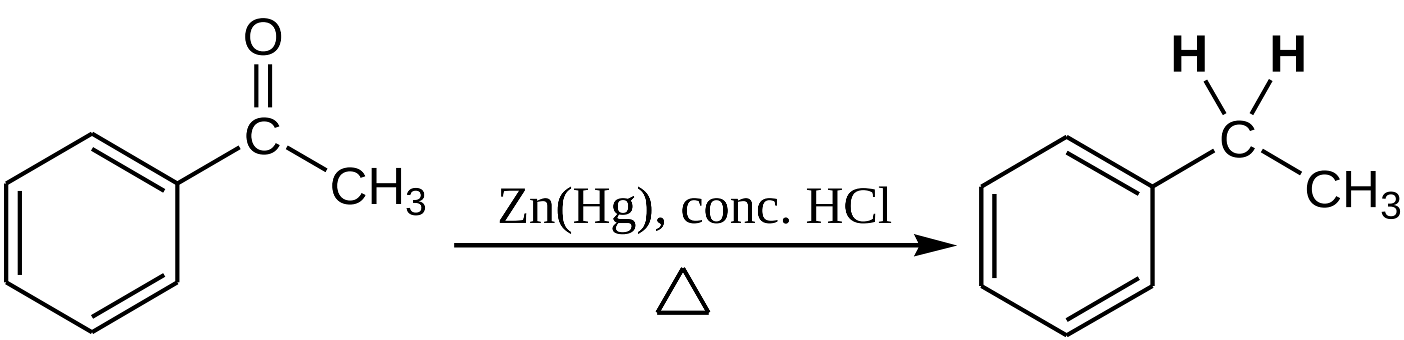
Examples:



Heptanal *n*-Heptane (72%)



Cyclohexanone Cyclohexane (75%)

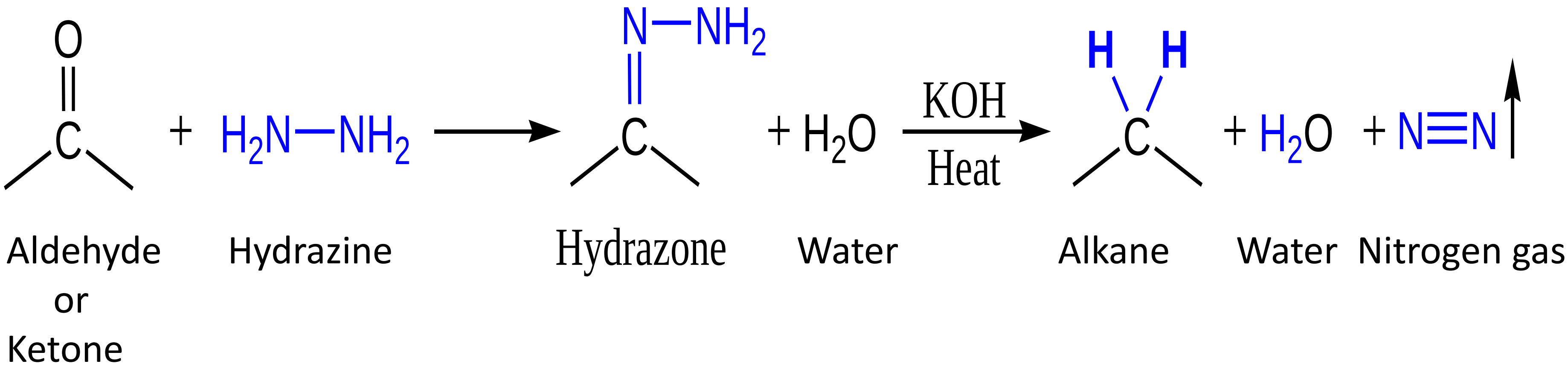


Acetophenone 1-Ethylbenzene

Reaction of Aldehydes and Ketones

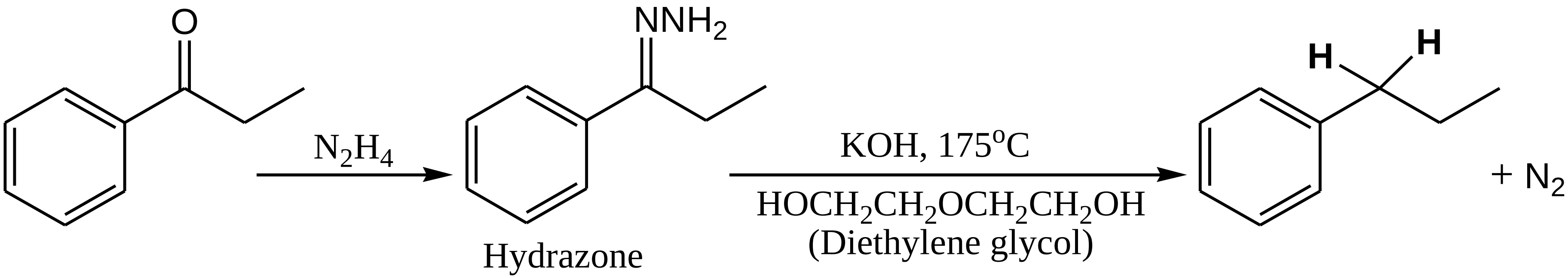
ii) Wolff–Kishner reduction:

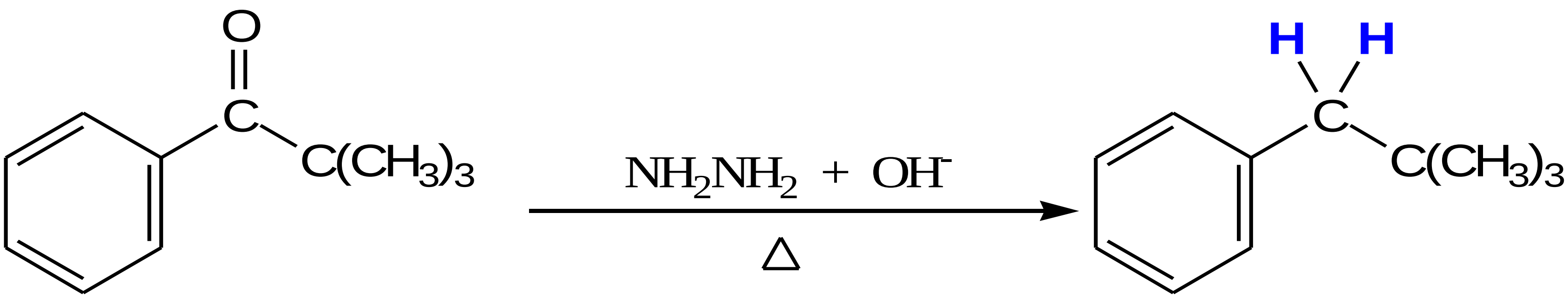
Compounds that cannot survive treatment with hot acid can be deoxygenated using the **Wolff–Kishner reduction.** The ketone or aldehyde is converted to its **hydrazone**, which is **heated** with Hydrazine **(NH_2NH_2)**, and **strong base** such as **KOH**. Ethylene glycol, diethylene glycol, or another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

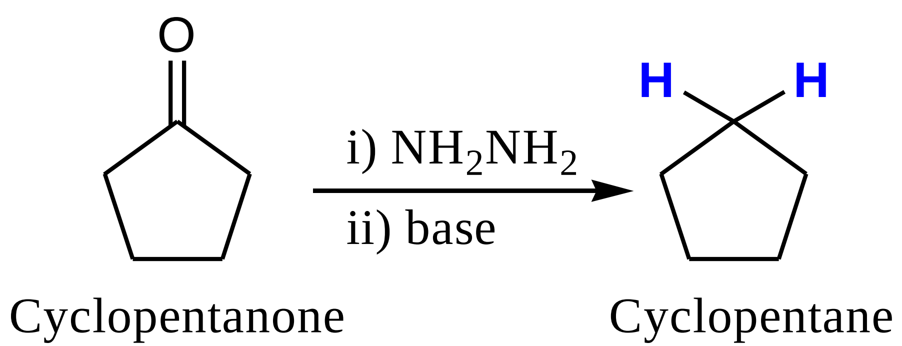


Reaction of Aldehydes and Ketones

Examples:

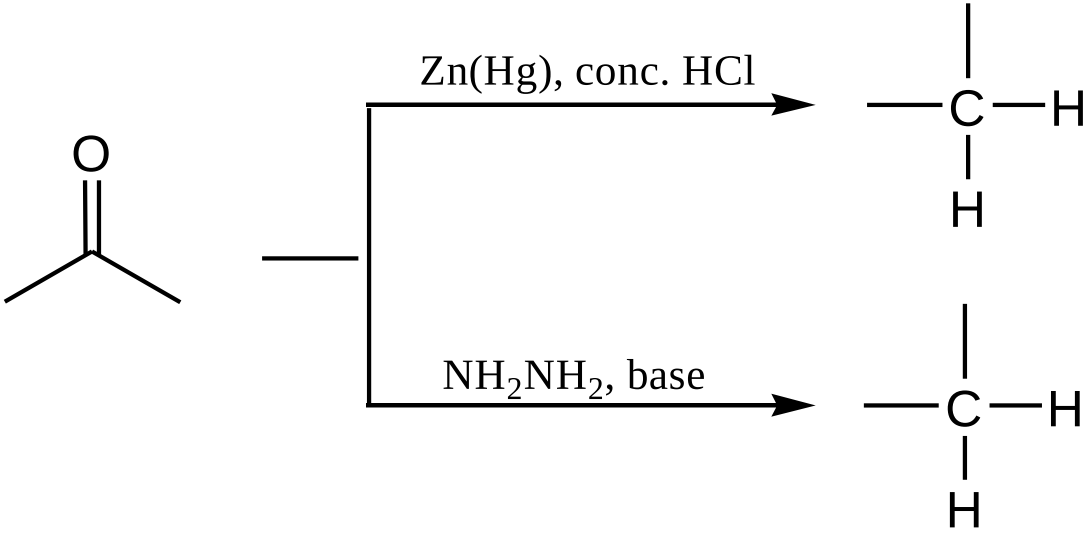






Reaction of Aldehydes and Ketones

Summary:



Clemmensen reduction

for compounds sensitive to base

Wolff-Kishner reduction

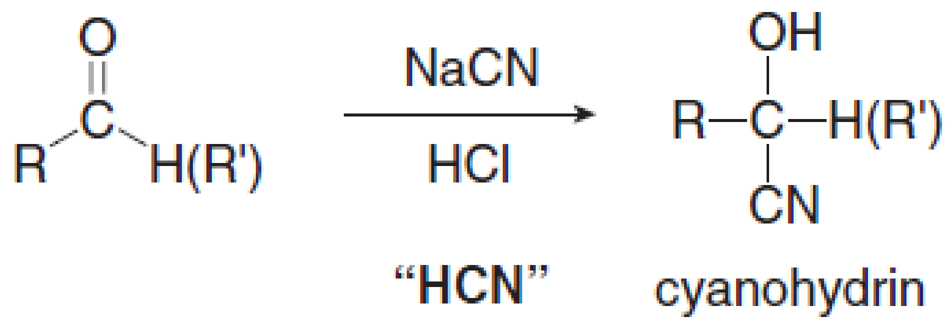
for compounds sensitive to acid

Reaction of Aldehydes and Ketones

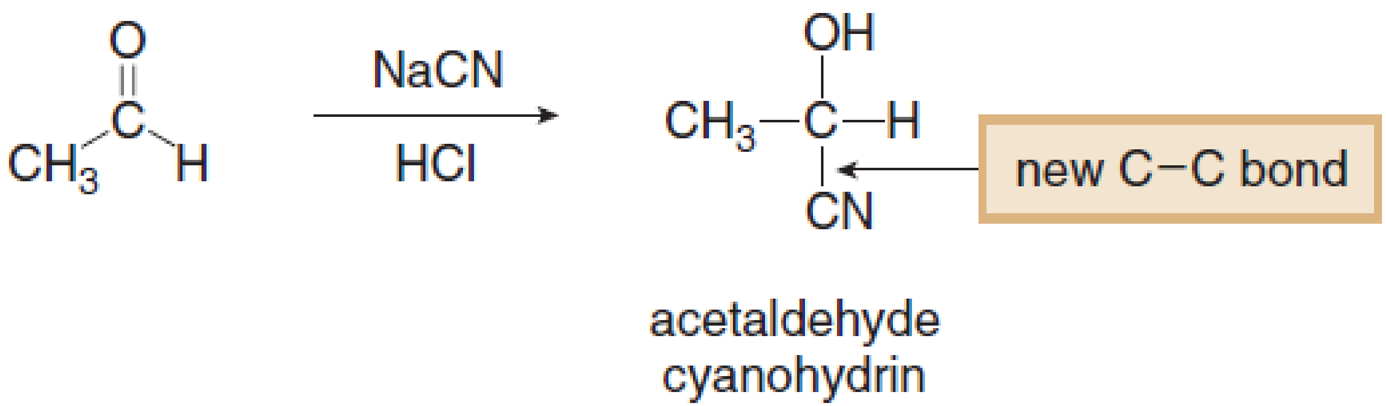
d) Nucleophilic Addition of CN^- :

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

Nucleophilic addition of HCN

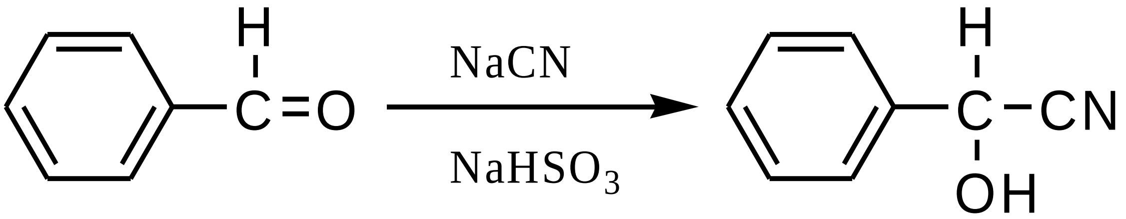


Example

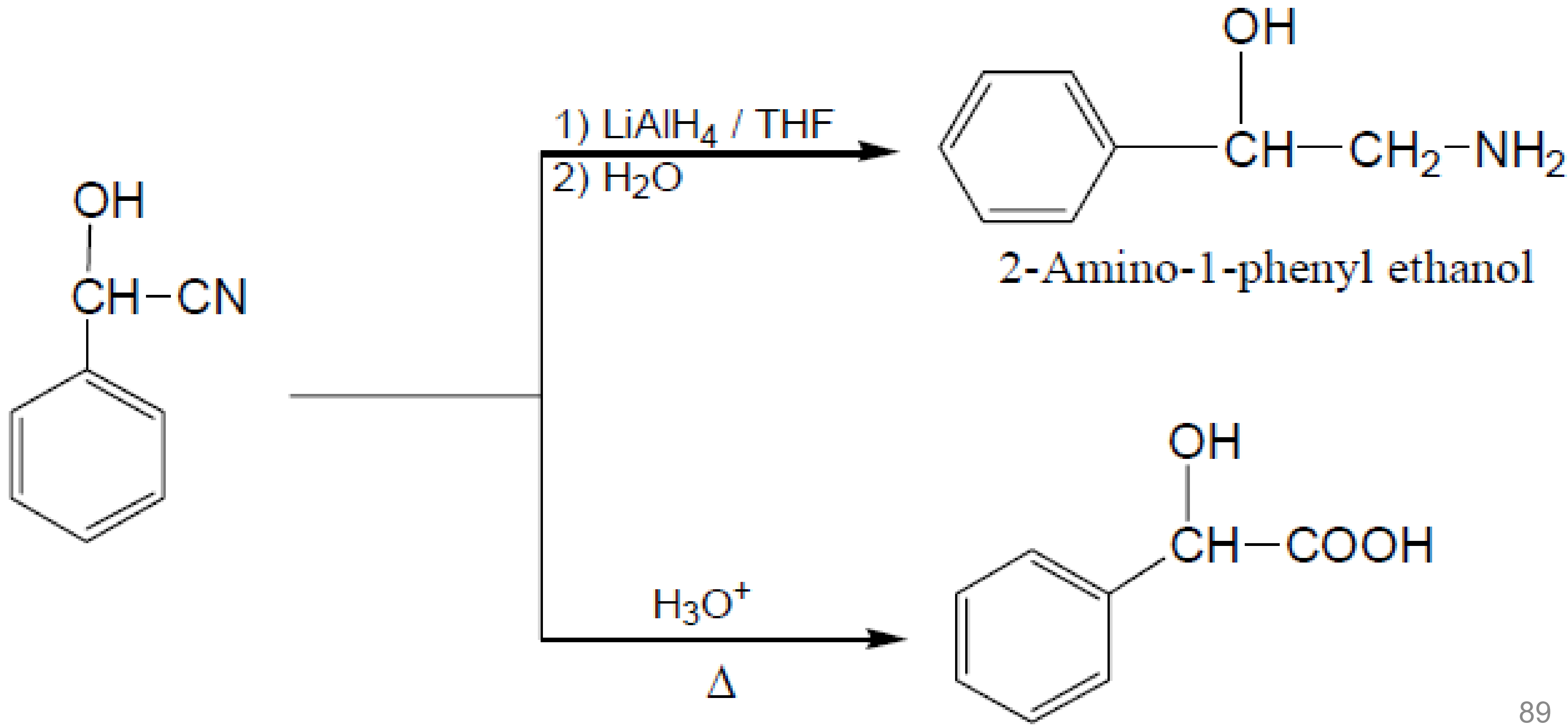


Reaction of Aldehydes and Ketones

Examples:



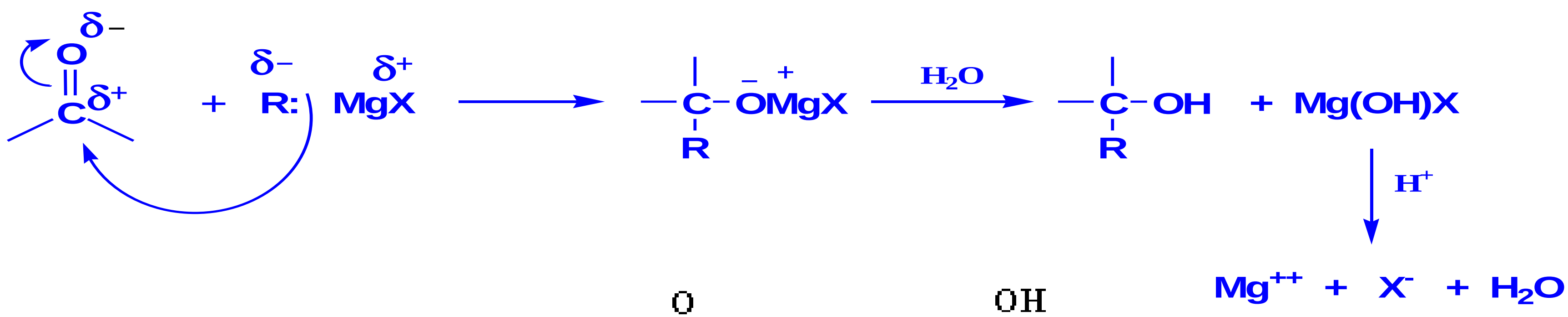
Benzaldehyde Mandelonitrile

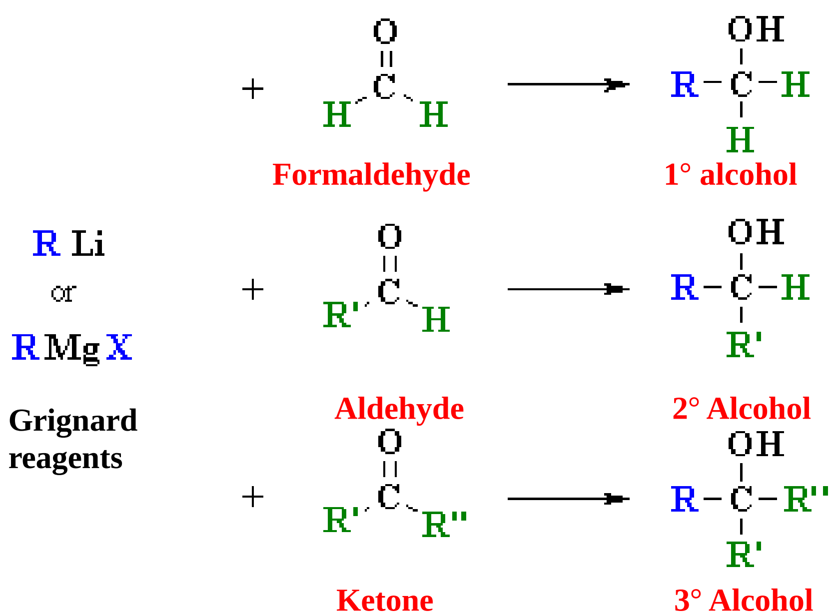


Reaction of Aldehydes and Ketones

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

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



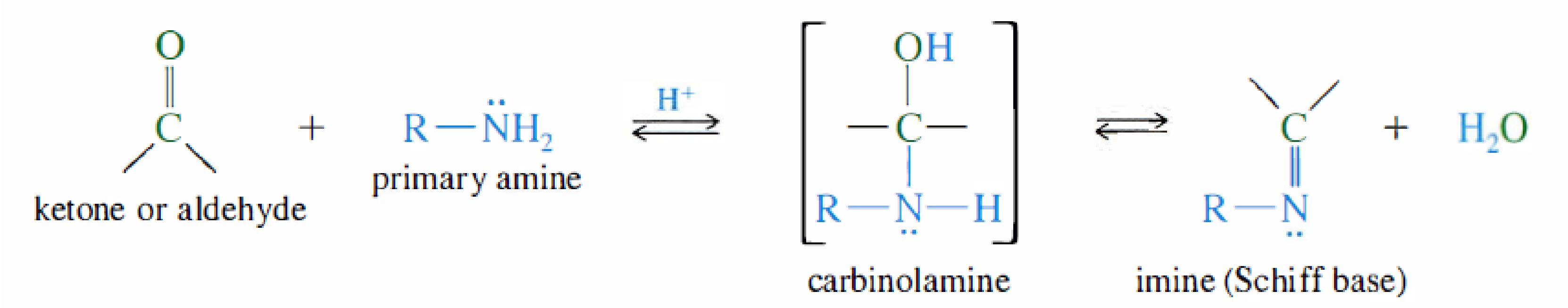


Reaction of Aldehydes and Ketones

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

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

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



Reaction of Aldehydes and Ketones

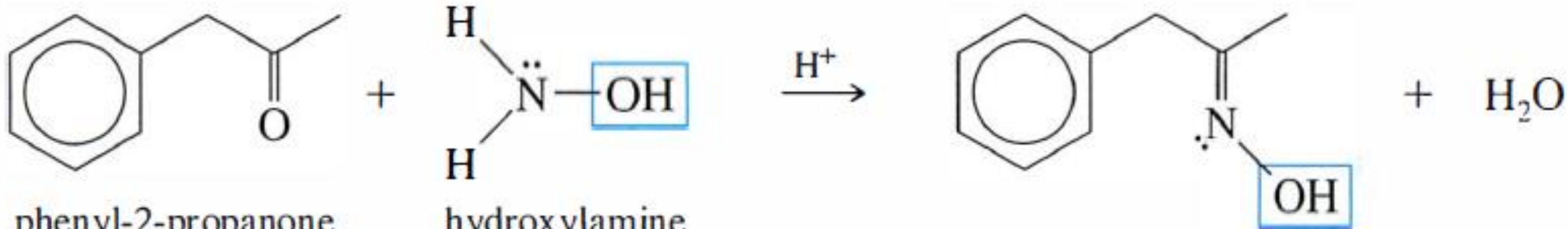
Addition of derivatives of Ammonia (Formation of imine):

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

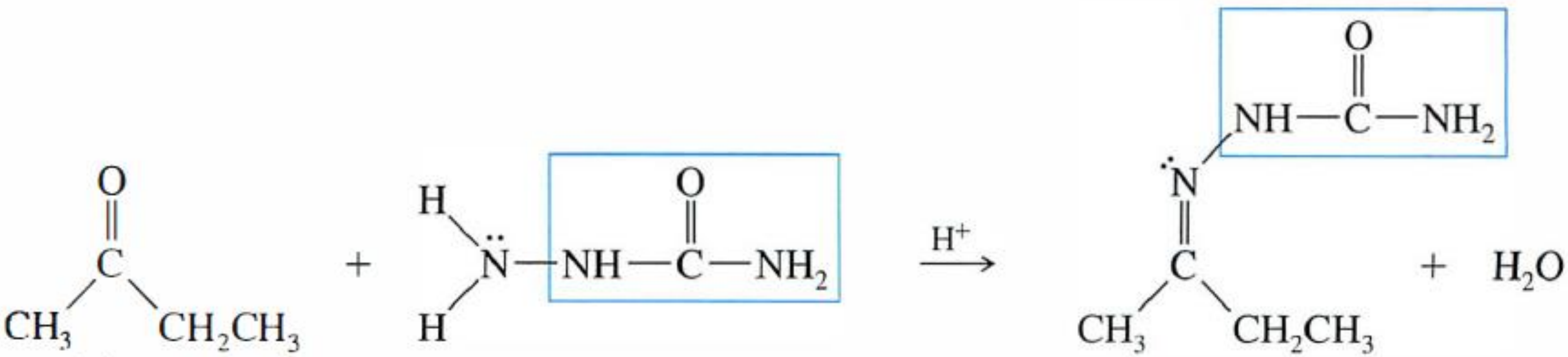
Z in Z—NH₂	*Reagent*	*Product*
—H	$H_2\ddot{N}{-}\boxed{H}$ ammonia	$>C{=}\ddot{N}{-}\boxed{H}$ an imine
—R	$H_2\ddot{N}{-}\boxed{R}$ primary amine	$>C{=}\ddot{N}{-}\boxed{R}$ an imine (Schiff base)
—OH	$H_2\ddot{N}{-}\boxed{OH}$ hydroxylamine	$>C{=}\ddot{N}{-}\boxed{OH}$ an oxime
$—NH_2$	$H_2\ddot{N}{-}\boxed{NH_2}$ hydrazine	$>C{=}\ddot{N}{-}\boxed{NH_2}$ a hydrazone
—NHPh	$H_2\ddot{N}{-}\boxed{NHPh}$ phenylhydrazine	$>C{=}\ddot{N}{-}\boxed{NHPh}$ a phenylhydrazone
$—NHC(=O)NH_2$	$H_2\ddot{N}{-}\boxed{NH{-}C(=O){-}NH_2}$ semicarbazide	$>C{=}\ddot{N}{-}\boxed{NH{-}C(=O){-}NH_2}$ a semicarbazone

Reaction of Aldehydes and Ketones

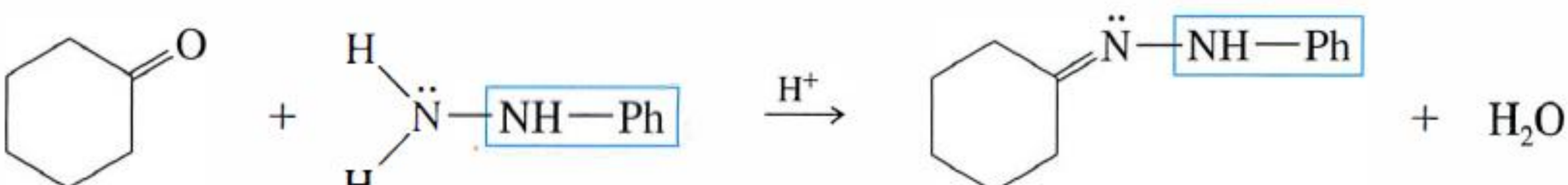
Examples:



phenyl-2-propanone hydroxylamine phenyl-2-propanone oxime



2-butanone semicarbazide 2-butanone semicarbazone

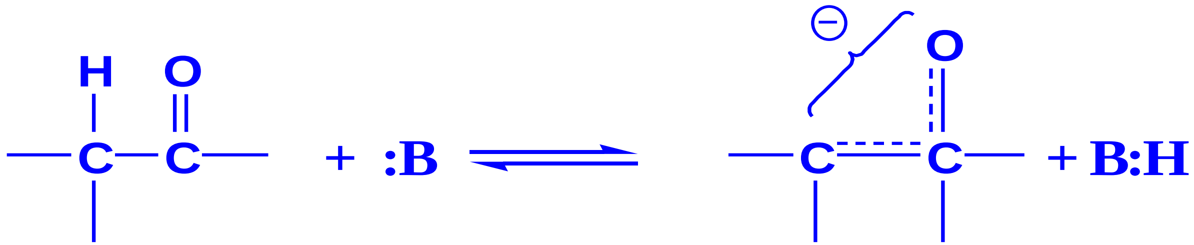


cyclohexanone phenylhydrazine cyclohexanone phenylhydrazone

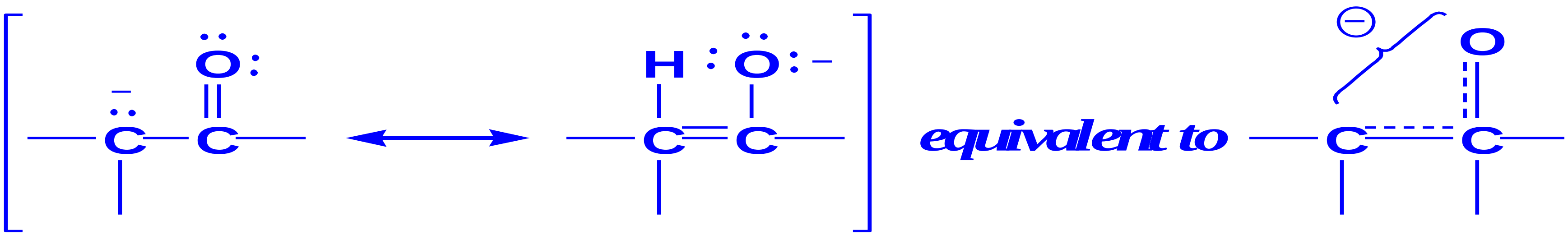
Reaction of Aldehydes and Ketones

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

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



(I)

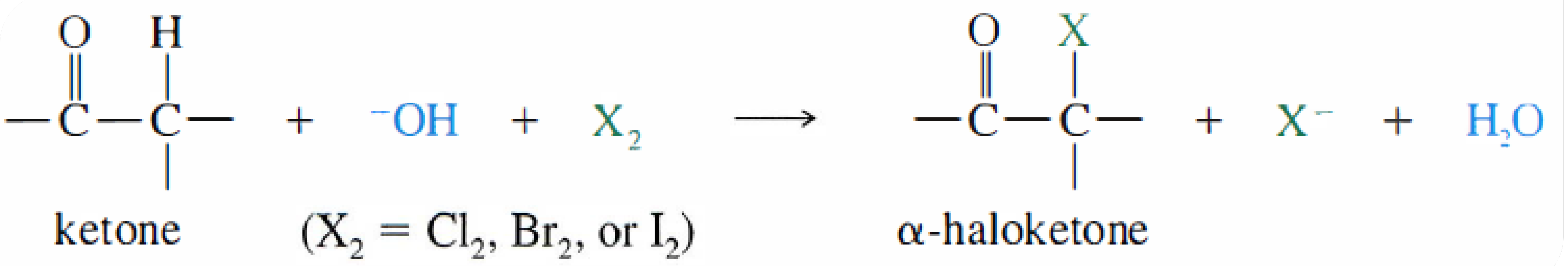


keto form ***Enol form*** **(I)**

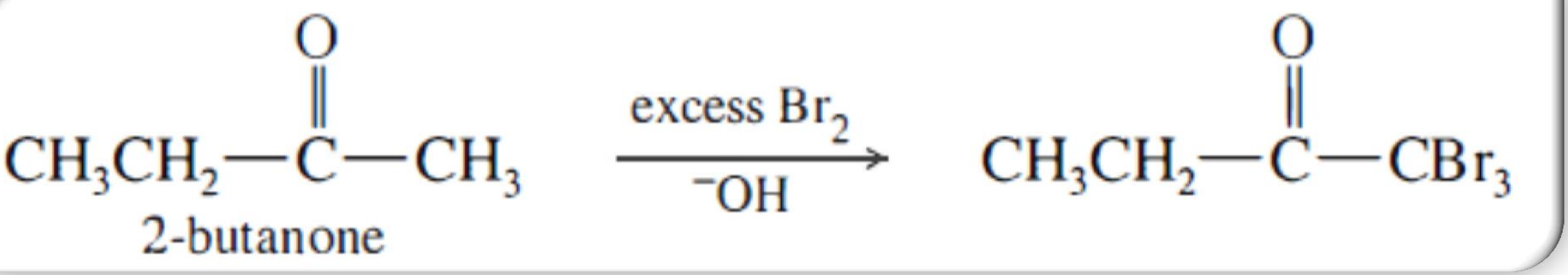
Reaction of Aldehydes and Ketones

a) Halogenation of ketones:

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

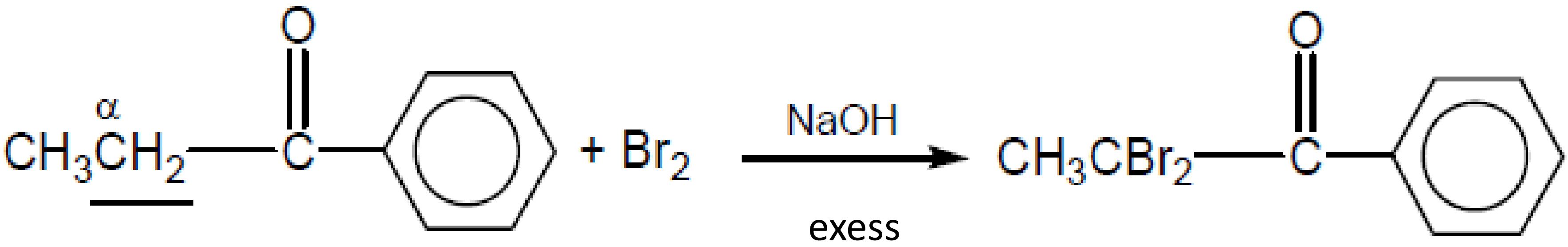


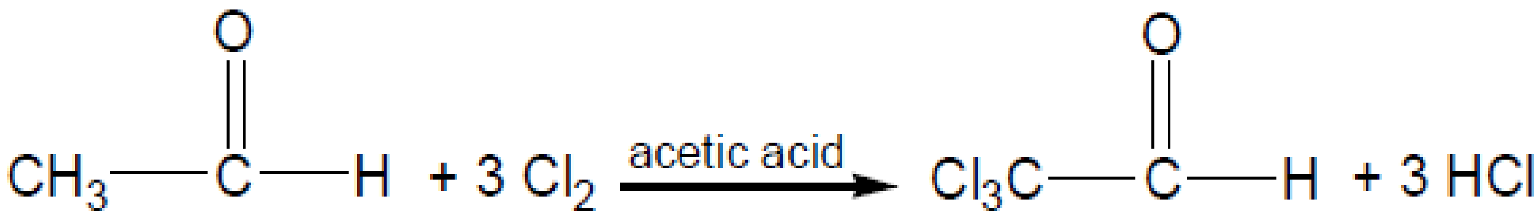
Examples:

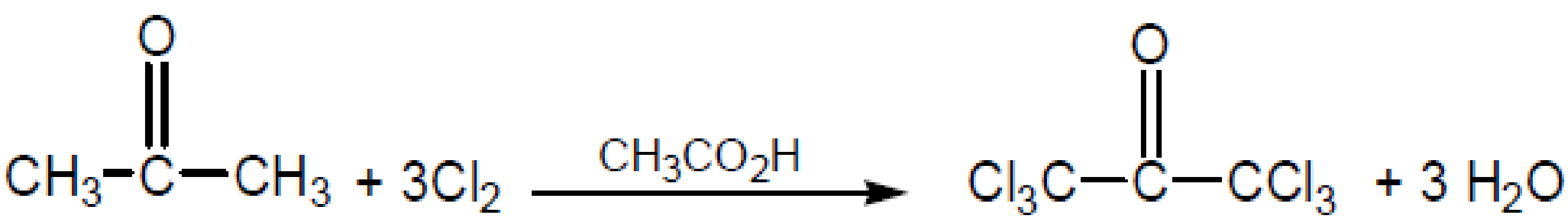


Reaction of Aldehydes and Ketones

Examples:





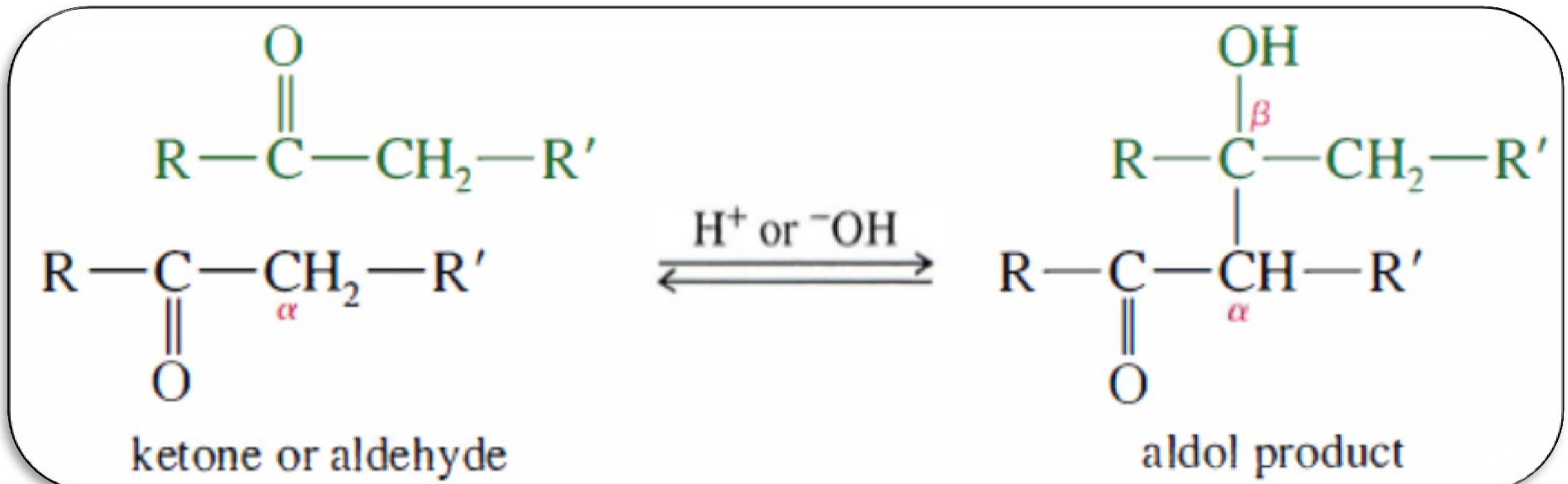


Reaction of Aldehydes and Ketones

b) Aldol coandensation:

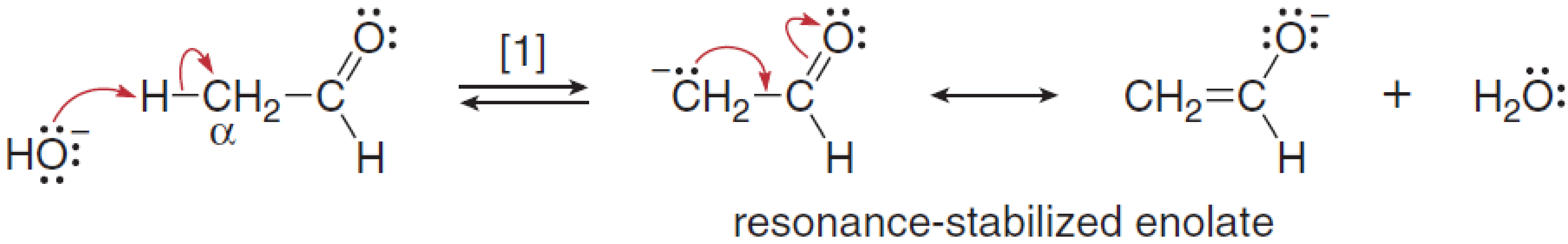
☞ Under the influence of **dilute base** or **dilute acid**, two molecules of an aldehyde or a ketone, which **contained α-hydrogen** , may combine to form a **β-Hydroxy aldehyde** or **β-Hydroxy ketone**. This reaction is called the **Aldol condensation**.

[redacted]

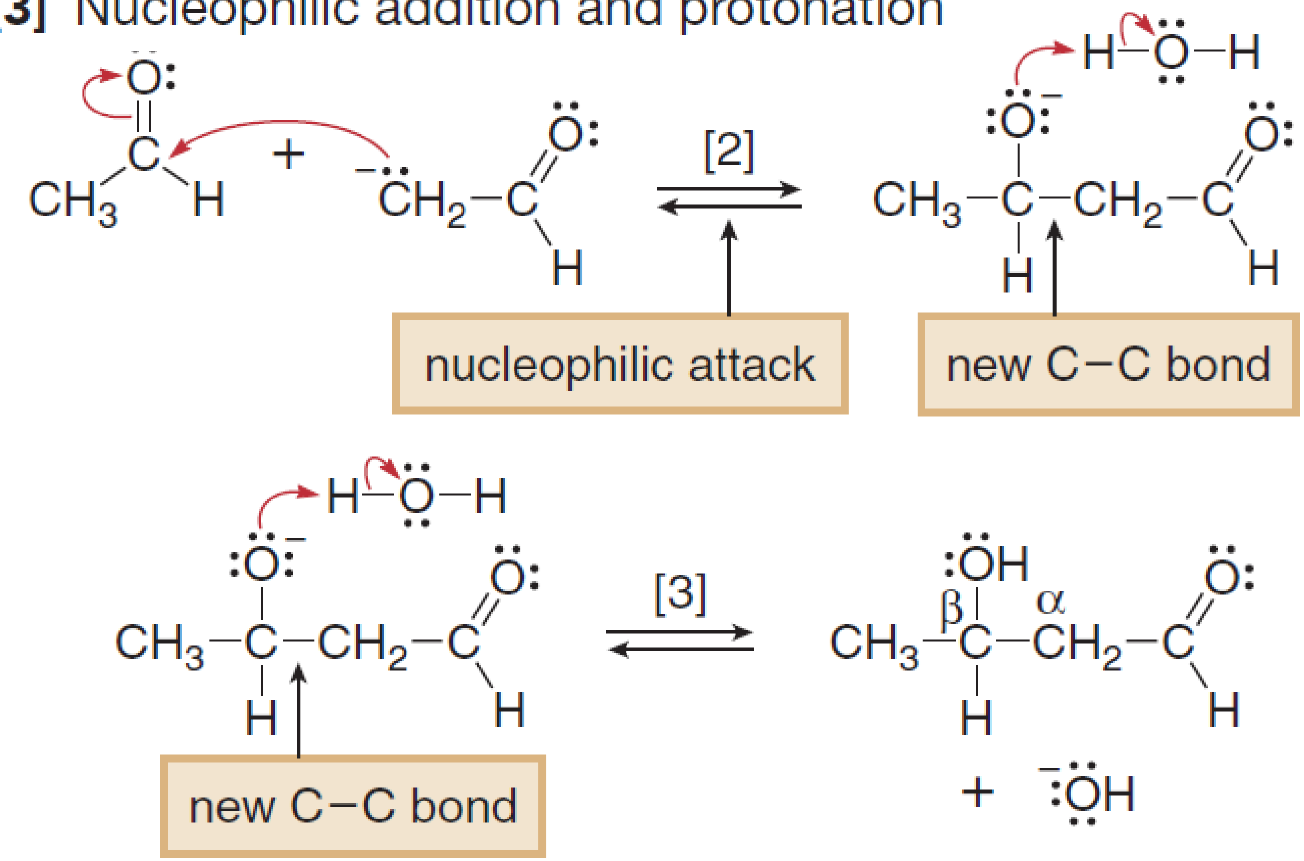


Mechanism:

Step [1] Formation of a nucleophilic enolate



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



Reaction of Aldehydes and Ketones

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

- ***For example:***

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

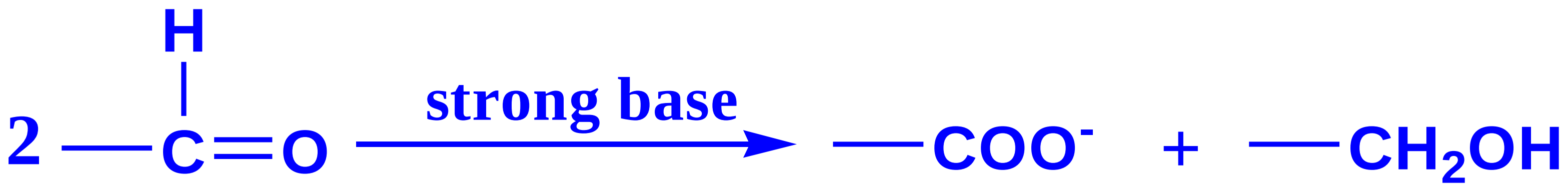
$\xrightarrow{\text{dilute } OH^-}$ **No reaction**

No α-hydrogen atoms

Reaction of Aldehydes and Ketones

Cannizzaro reaction:

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



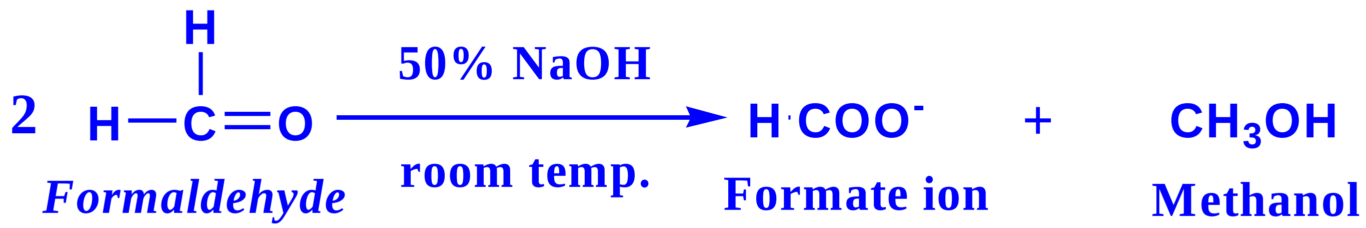
An aldehyde with no α–hydrogen

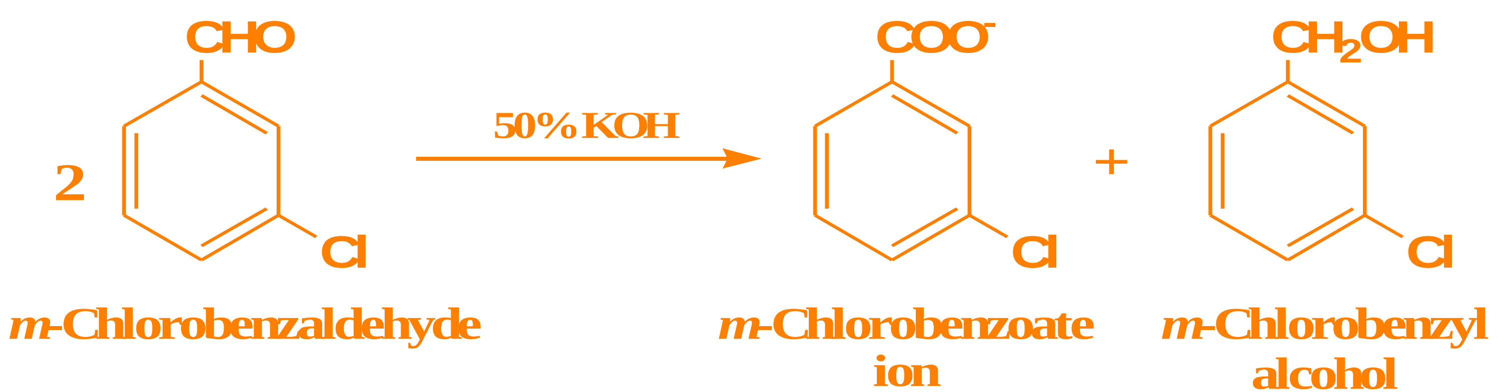
Acid salt

Alcohol

Reaction of Aldehydes and Ketones

Examples:



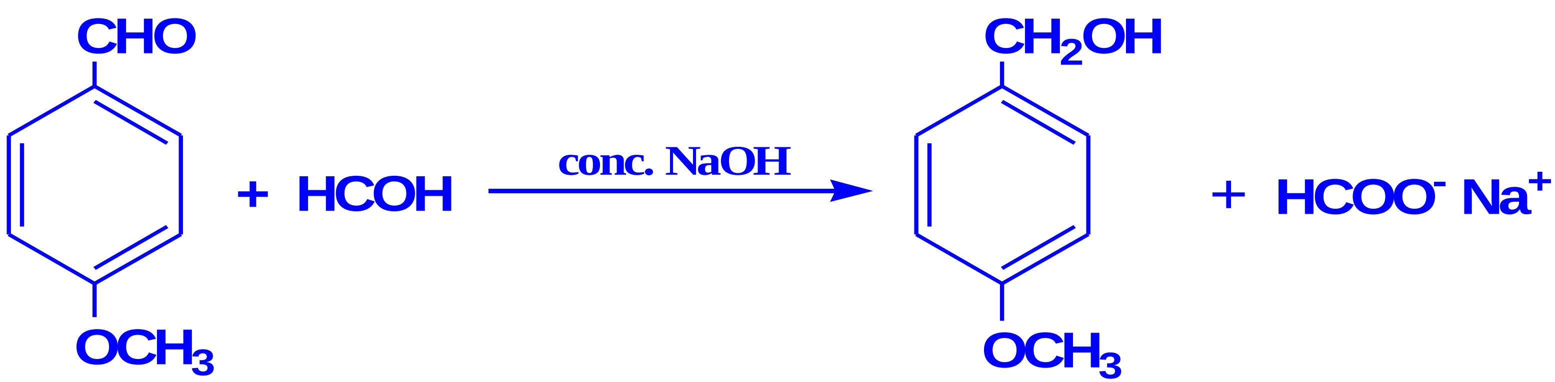


Reaction of Aldehydes and Ketones

Crossed Cannizzaro reaction

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

$$ArCHO + HCOH \xrightarrow{\text{conc. NaOH}} ArCH_2OH + HCOO^-Na^+$$



Anisaldehyde
***m*-Methoxybenzaldehyde**

***m*-Methoxybenzyl alcohol**