

Organic Chemistry for Biology Students

CHAPTER ONE

Lecture 1

Alkanes and Cycloalkanes

by

Dr. Omar Abdulateef

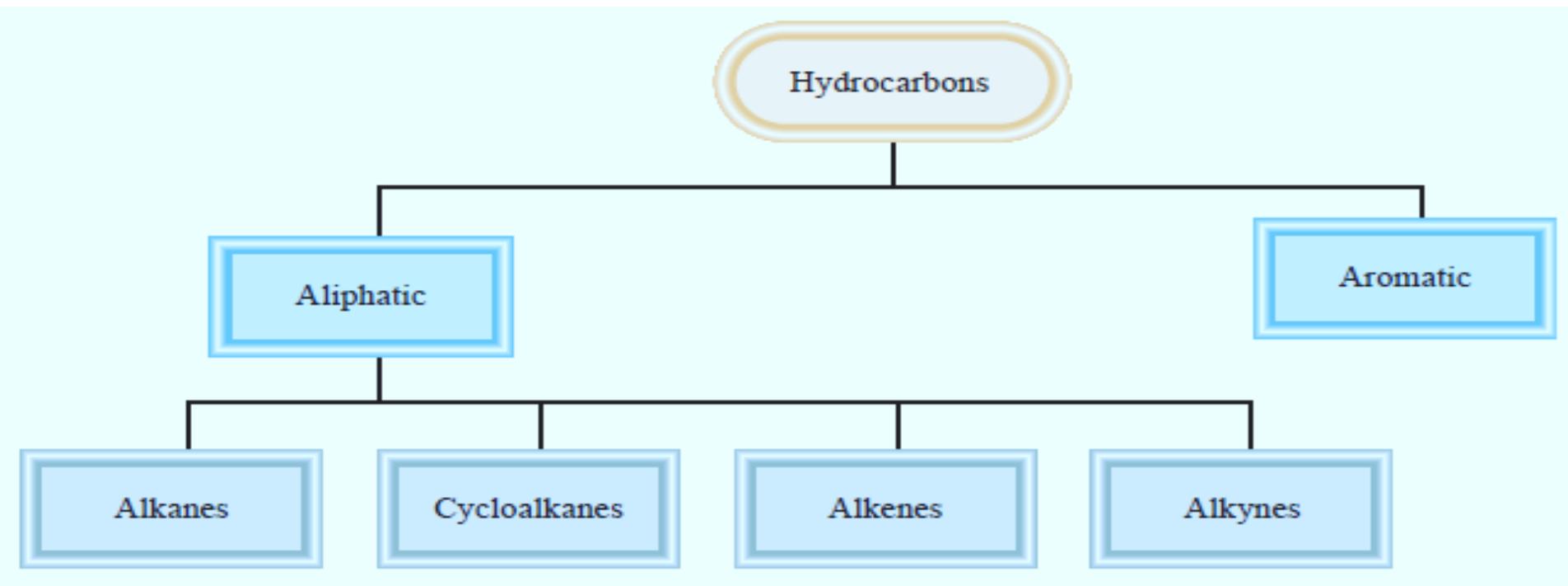
2020-2021

Introduction to Organic Chemistry

The branch of chemistry that deals with **carbon compounds** is **Organic Chemistry**. **The hydrocarbons** are used as fuels for domestic and industrial heating, for generating electricity and powering internal combustion engines, and as starting materials for the chemical industry. Biomolecules such as proteins, carbohydrates, fats, and nucleic acids are organic compound. Wool, cotton and silk, in addition to nylon and acrylates, ...etc. (the raw materials in cloths and furniture industry), are organic compounds. All plastic materials, and some dyes and paints are organic compounds. Detergents, drugs, and deferent pharmaceutical products and perfumes are basically organic compounds. Furthermore, some organic compounds with special structural properties, are recently incorporated in the industry of deferent electronic devices.

Hydrocarbons

The simplest type of organic compounds is the **hydrocarbons**, which contain only carbon and hydrogen atoms. Carbon can form more compounds than most other elements because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures. All organic compounds are derived from the **hydrocarbons** because they are made up of only **hydrogen and carbon**. On the basis of structure, hydrocarbons are divided into two main classes—**aliphatic** and **aromatic**. **Aliphatic hydrocarbons do not contain the benzene group, or the benzene ring**, whereas **aromatic hydrocarbons contain one or more benzene rings**.

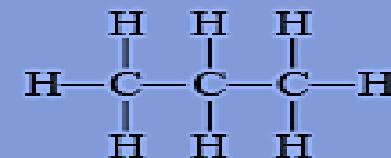
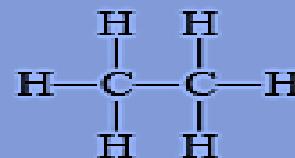
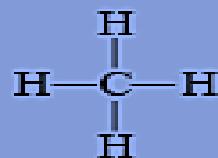


Aliphatic Hydrocarbons

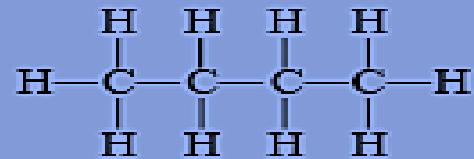
Aliphatic hydrocarbons are divided into **alkanes**, **cycloalkanes**, **alkenes**, and **alkynes**

Alkanes

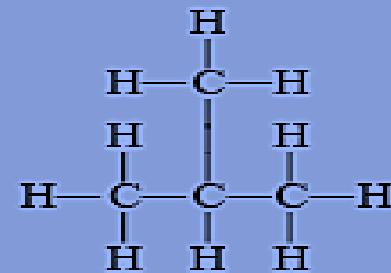
Alkanes are hydrocarbons that have the general formula C_nH_{2n+2} , where $n = 1, 2, 3 \dots$. The essential characteristic of alkanes is that only single covalent bonds are present. The alkanes are known as **saturated hydrocarbons** because they contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present.



Structures of the first four alkanes. Note that butane can exist in two structurally different forms, called structural isomers.



n-Butane



Isobutane

Table 1.1 shows the melting and boiling points of the straight-chain isomers of the first 10 alkanes. The first four are gases at room temperature; and pentane through decane are liquids. As molecular size increases, so does the boiling point.

Table 1.1

Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms	Melting Point (°C)	Boiling Point (°C)
Methane	CH ₄	1	-182.5	-161.6
Ethane	CH ₃ —CH ₃	2	-183.3	-88.6
Propane	CH ₃ —CH ₂ —CH ₃	3	-189.7	-42.1
Butane	CH ₃ —(CH ₂) ₂ —CH ₃	4	-138.3	-0.5
Pentane	CH ₃ —(CH ₂) ₃ —CH ₃	5	-129.8	36.1
Hexane	CH ₃ —(CH ₂) ₄ —CH ₃	6	-95.3	68.7
Heptane	CH ₃ —(CH ₂) ₅ —CH ₃	7	-90.6	98.4
Octane	CH ₃ —(CH ₂) ₆ —CH ₃	8	-56.8	125.7
Nonane	CH ₃ —(CH ₂) ₇ —CH ₃	9	-53.5	150.8
Decane	CH ₃ —(CH ₂) ₈ —CH ₃	10	-29.7	174.0

Alkane Nomenclature

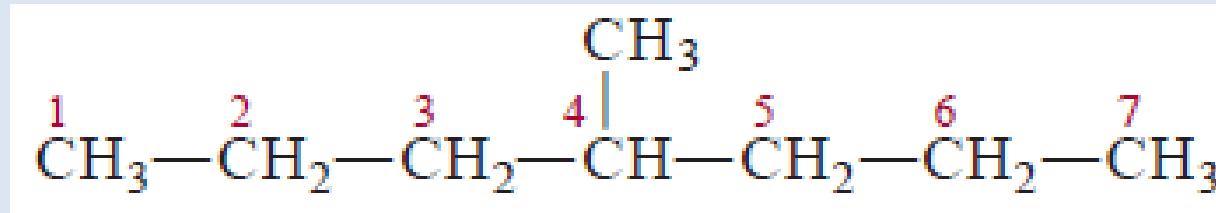
The nomenclature of alkanes and all other organic compounds is based on the recommendations of the **International Union of Pure and Applied Chemistry (IUPAC)**. The first four alkanes (methane, ethane, propane, and butane) have nonsystematic names. As Table 1.2 shows, the number of carbon atoms is reflected in the Greek prefixes for the alkanes containing 5 to 10 carbons.

Table 1.2

Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms
Methane	CH_4	1
Ethane	CH_3-CH_3	2
Propane	$\text{CH}_3-\text{CH}_2-\text{CH}_3$	3
Butane	$\text{CH}_3-(\text{CH}_2)_2-\text{CH}_3$	4
Pentane	$\text{CH}_3-(\text{CH}_2)_3-\text{CH}_3$	5
Hexane	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}_3$	6
Heptane	$\text{CH}_3-(\text{CH}_2)_5-\text{CH}_3$	7
Octane	$\text{CH}_3-(\text{CH}_2)_6-\text{CH}_3$	8
Nonane	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}_3$	9
Decane	$\text{CH}_3-(\text{CH}_2)_8-\text{CH}_3$	10

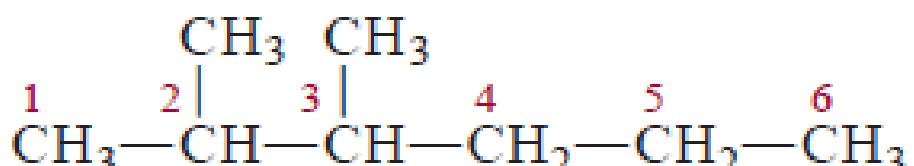
The IUPAC Rules for Alkane Nomenclature

1. نحدد السلسلة الام (وهي أطول سلسلة لذرات الكربون في الجزيء) و من ثم ترقم ذرات ال C مع مراعاة ان تأخذ ذرة C المترفرعة اصغر الارقام و يسمى المركب حسب عدد ذرات C المكونة لتلك السلسلة (راجع الجدول في السلايد السابق). فمثلا يسمى المركب التالي **heptane** لأن السلسلة الأطول مكونة من سبعة ذرات C

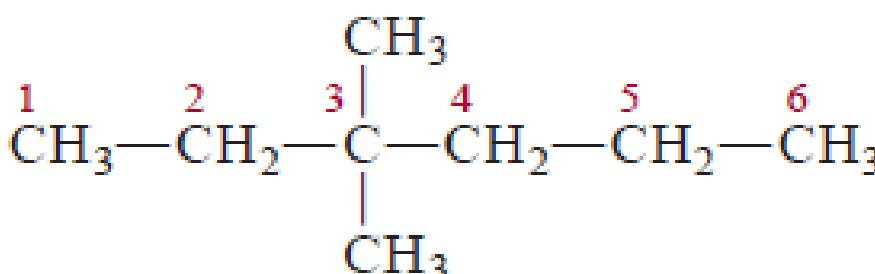


2. الالكان المترفرع: يسمى التفرع بمجموعة الالكيل (**alkyl group**) و حسب عدد ذرات C لذلك التفرع. فإذا كان مكون من ذرة C واحدة يسمى **methyl** وإذا تكون من ذرتين C فيسمى **ethyl** .. وهكذا (أي يحذف المقطع **-ane** من نهاية اسم الالكان الأصلي و يستبدل بالقطع **-yl** - لينتاج اسم مجموعة الالكيل المترفرعة من السلسلة الام). وبذلك يصبح اسم المركب أعلاه **4-Methylheptane**.

3. في حالة وجود اكثر من مجموعة الالكيل فرعية و من نفس النوع نستخدم عندها البادئ (**-di** لمجموعتين) و (**-tri** لثلاث مجامي) و (**-tetra**- لأربع مجامي) و (**-penta** لخمسة مجامي) ... وهكذا وذلك قبل اسم المجموعة مع كتابة رقم ذرة C التي تحمل ذلك التفرع لتحديد موقعها على السلسلة الام. كما في المثالين الآتيين:

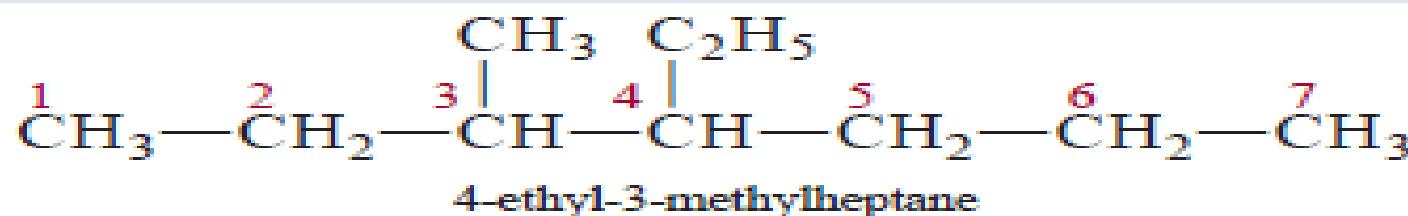


2,3-dimethylhexane



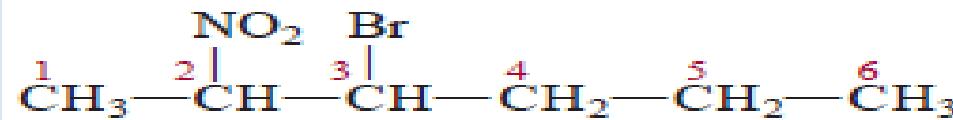
3,3-dimethylhexane

اما اذا كانت التفرعات عبارة عن مجاميع الكيل مختلفة فعندئذ يكتب اسم كل مجموعة مسبوقة بالرقم الدال على موقعها على السلسلة مع مراعاة التسلسل الابجدي للحروف في اسبقية كتابتها , كما في المثال الاتي:



4. في حالة وجود مجاميع معرفة على الالكان مثل NO_2 , Br , Cl , F وغيرها ، فعندما يكتب اسم المجموعة المعرفة مسبوقة برقم ذرة C الحاملة لها مع مراعاة التسلسل الابجدي في اسبقية كتابتها ضمن الاسم (مع مراعاة القاعدة العامة في ان اتجاه الترقيم للسلسلة الا ان يجب ان يعطى المجاميع المعرفة اصغر الأرقام).

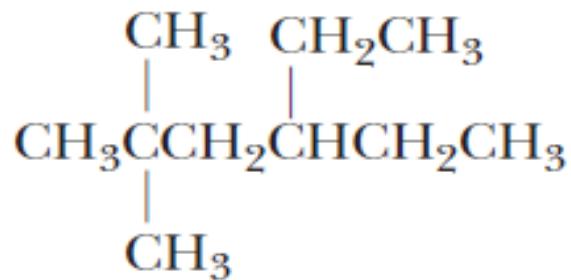
3-bromo-2-nitrohexane



Names of Common Substituent Groups

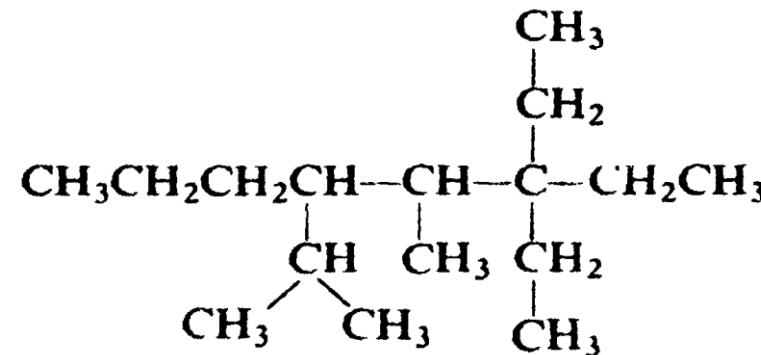
Functional Group	Name
—NH ₂	Amino
—F	Fluoro
—Cl	Chloro
—Br	Bromo
—I	Iodo
—NO ₂	Nitro

5- The prefixes *di-*, *tri-*, *tetra-*, and so on are not included in alphabetizing. Neither are the hyphenated prefixes *sec-* and *tert-*. “Iso,” as in isopropyl, is included in alphabetizing. **Alphabetize the names of the substituents first, and then insert the prefix.** In the following example[compound(I)], the alphabetizing parts are **ethyl** and **methyl**, **not** ethyl and **dimethyl**:



4-Ethyl-2,2-dimethylhexane
(not 2,2-dimethyl-4-ethylhexane)

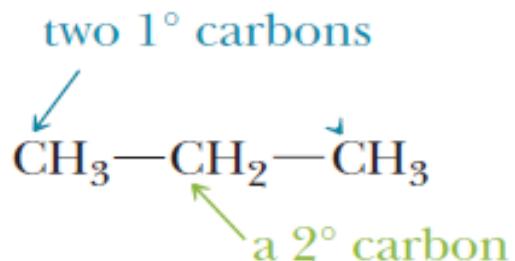
Compound (I)



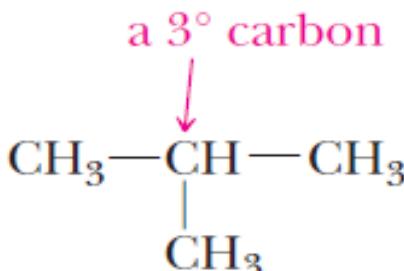
3,3-Diethyl-5-isopropyl-4-methyloctane

Classification of Carbon and Hydrogen Atoms

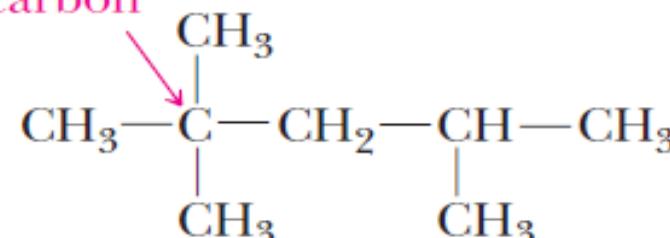
We classify a carbon atom as **primary (1°)**, **secondary (2°)**, **tertiary (3°)**, or **quaternary (4°)**, depending on the number of carbon atoms bonded to it.



Propane



2-Methylpropane



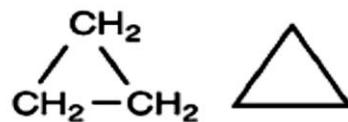
2,2,4-Trimethylpentane

Table 1.3: Names of the Most Common Alkyl Groups

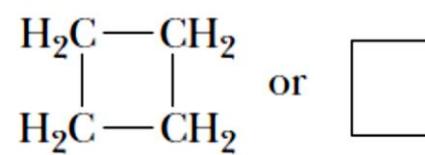
Name	Condensed Structural Formula	Name	Condensed Structural Formula
methyl	$-\text{CH}_3$	isobutyl	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$
ethyl	$-\text{CH}_2\text{CH}_3$	<i>sec</i> -butyl	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
propyl	$-\text{CH}_2\text{CH}_2\text{CH}_3$	<i>tert</i> -butyl	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}(\text{CH}_3)_3 \\ \\ \text{CH}_3 \end{array}$
isopropyl	$-\text{CH}(\text{CH}_3)_2$	abbreviation for “secondary”	
butyl	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	abbreviation for “tertiary”	

Cycloalkanes

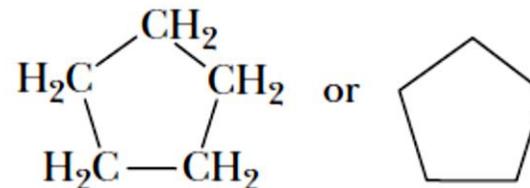
A hydrocarbon that contains carbon atoms joined to form a ring is called a cyclic hydrocarbon. When all carbons of the ring are saturated, we call the hydrocarbon a cycloalkane. Cycloalkanes of ring sizes ranging from 3 to over 30 abound in nature, and, in principle, there is no limit to ring size. Five-membered (**cyclopentane**) and six-membered (**cyclohexane**) rings are especially abundant in nature and have received special attention.



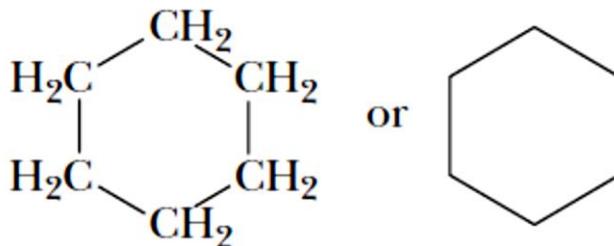
Cyclopropane



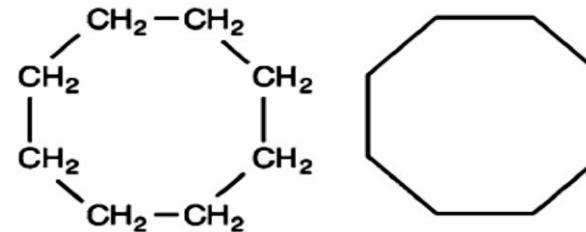
Cyclobutane



Cyclopentane



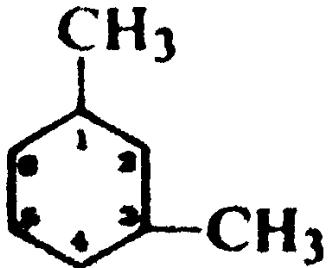
Cyclohexane



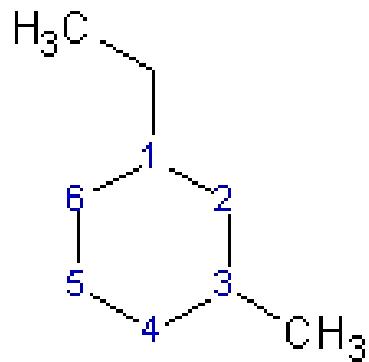
Cyclooctane

Cycloalkanes contain two fewer hydrogen atoms than an alkane with the same number of carbon atoms. For instance, compare the molecular formulas of cyclohexane (C_6H_{12}) and hexane (C_6H_{14}). The general formula of a cycloalkane is C_nH_{2n} .

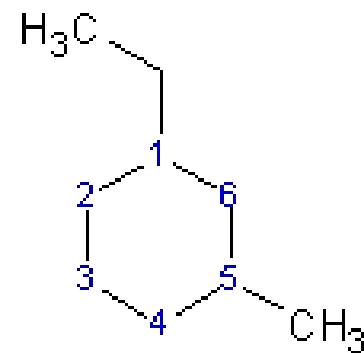
To name a cycloalkane, prefix the name of the corresponding open-chain hydrocarbon with **cyclo-**, and name each substituent on the ring. If there is only one substituent, there is no need to give it a number. If there are two substituents, number the ring by beginning with the substituent of lower alphabetical order. If there are three or more substituents, number the ring so as to give them the lowest set of numbers, and then list the substituents in alphabetical order.



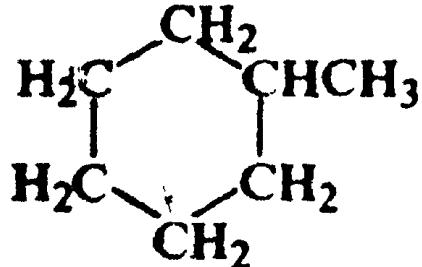
1,3-Dimethylcyclohexane



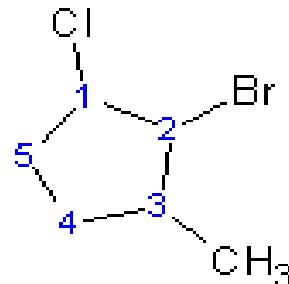
1-ethyl-3-methylcyclohexane



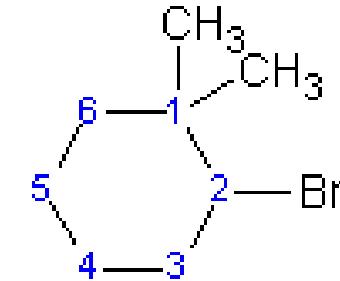
1-ethyl-5-methylcyclohexane



Methylcyclohexane

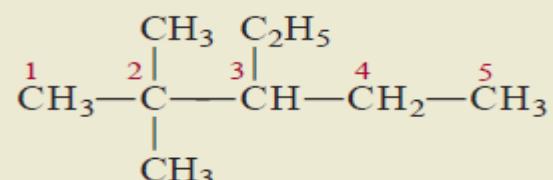


2-Bromo-1-chloro-3-methylcyclopentane

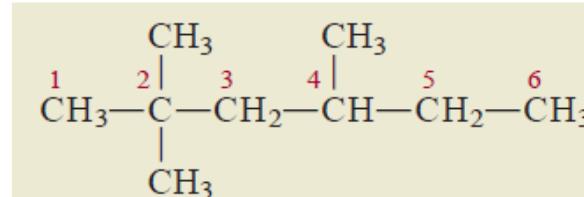


2-Bromo-1,1-dimethylcyclohexane

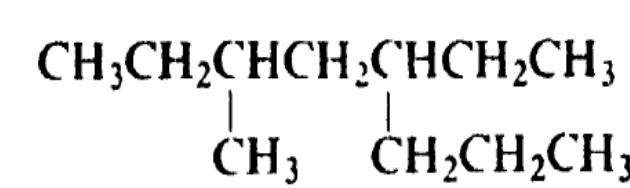
Examples:



3-ethyl-2,2-dimethylpentane



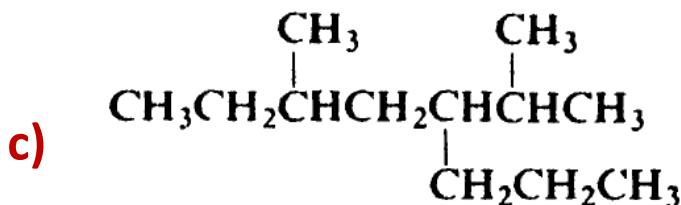
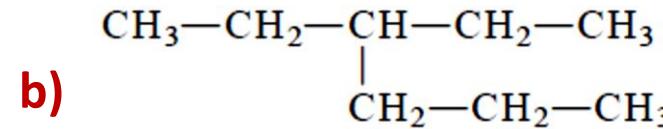
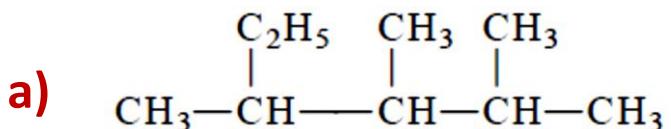
2,2,4-trimethylhexane



5-Ethyl-3-methyloctane

Problems:

1) Give the IUPAC name of the following compounds:



2) Give the structural formula of the following compounds:

a) 4-Ethyl-3,4-dimethylheptane

c) 1,4-Dimethylcyclohexane

b) 2,2,4-Trimethylpentane

d) 3-Isopropyl-1-methylcyclopentane

Organic Chemistry for Biology Students

CHAPTER ONE

Lecture 2

Alkanes and Cycloalkanes

Dr. Omar Abdulateef

NATURAL SOURCES OF ALKANES

The three major sources of alkanes (and cycloalkanes) throughout the world are the fossil fuels: **natural gas**, **petroleum**, and **coal**.

A. Natural Gas

Natural gas consists of approximately 90–95% methane, 5–10% ethane, and a mixture of other relatively low-boiling alkanes—chiefly propane, butane, and 2-methylpropane.

B. Petroleum

Petroleum is a thick, viscous liquid mixture of literally thousands of compounds, most of them hydrocarbons, formed from the decomposition of marine plants and animals. Petroleum and petroleum-derived products fuel automobiles, aircraft, and trains. They provide most of the greases and lubricants required for the machinery of our highly industrialized society. Furthermore, petroleum, along with natural gas, provides close to 90% of the organic raw materials used in the synthesis and manufacture of synthetic fibers, plastics, detergents, drugs, dyes, and a multitude of other products.

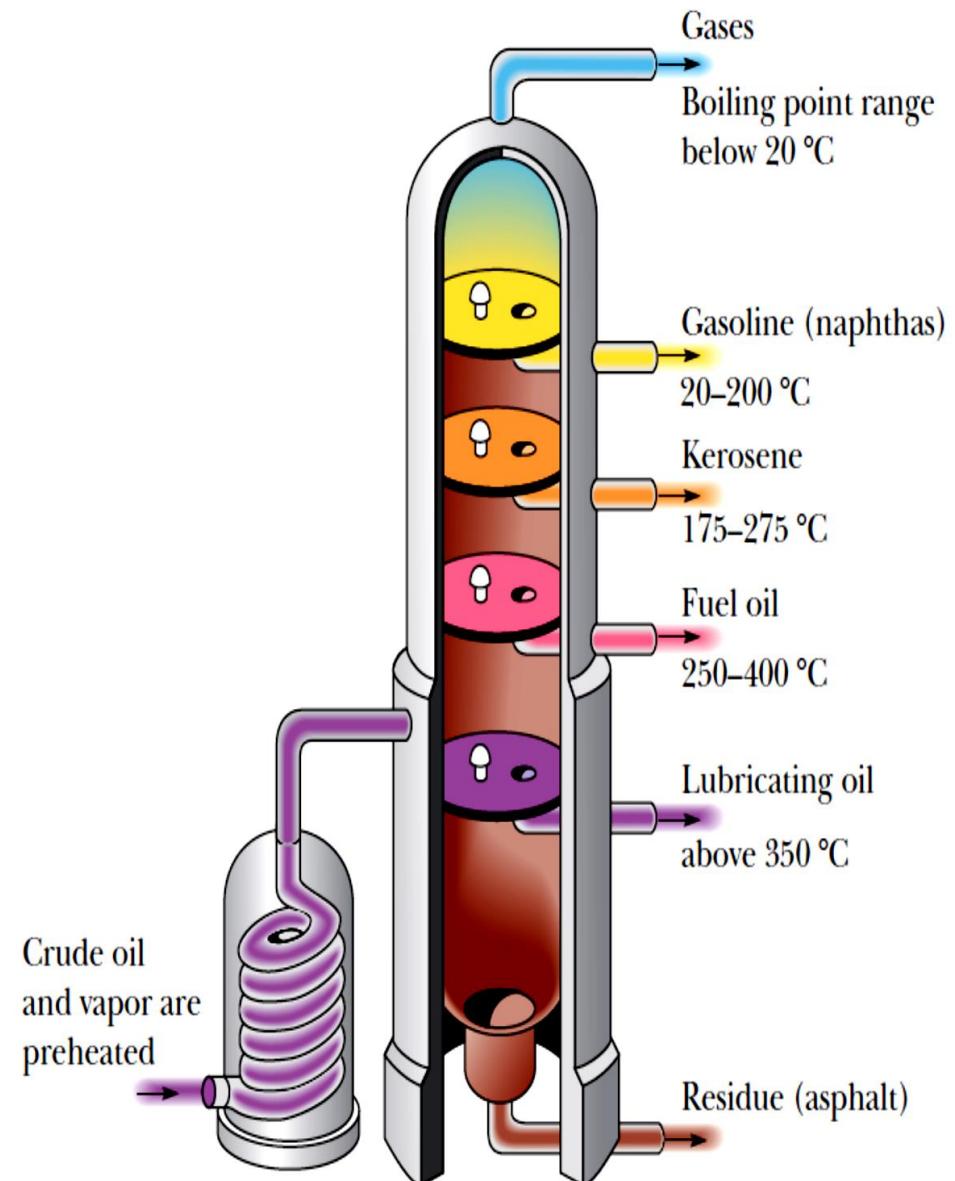
C. Coal

Coal can be used as a raw material for the production of organic compounds. **Synthesis gas** is a mixture of carbon monoxide and hydrogen in varying proportions. **Synthesis gas is prepared by passing steam over coal.**

PETROLEUM REFINING PROCESS

The fundamental separation process utilized in refining petroleum is **fractional distillation**. Practically all crude oil that enters a refinery goes to distillation units, where it is heated to temperatures as high as 370 to 425 °C and separated into fractions. Each fraction contains a mixture of hydrocarbons that boils within a particular range:

1. **Gases boiling below 20 °C** are taken off at the top of the distillation column. This fraction is a mixture of low-molecular-weight hydrocarbons, predominantly propane, butane, and 2-methylpropane, substances that can be liquefied under pressure at room temperature. The liquefied mixture, known as liquefied petroleum gas (LPG), can be stored and shipped in metal tanks and is a convenient source of gaseous fuel for home heating and cooking.

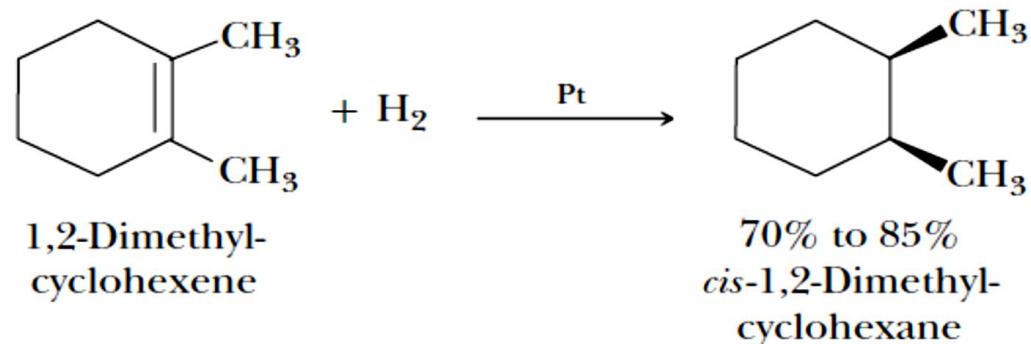
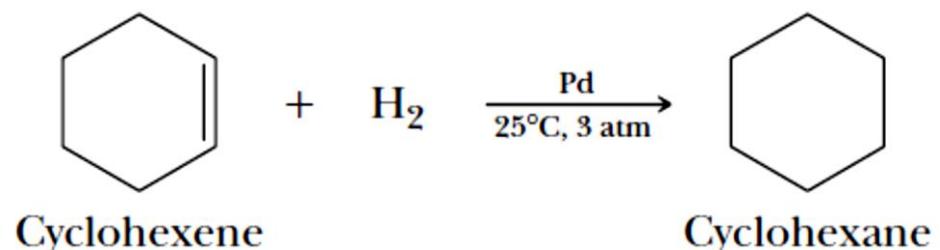
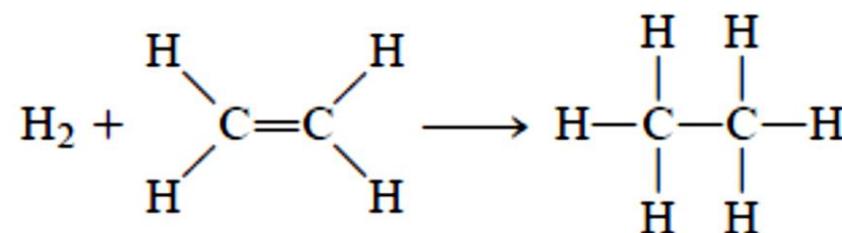
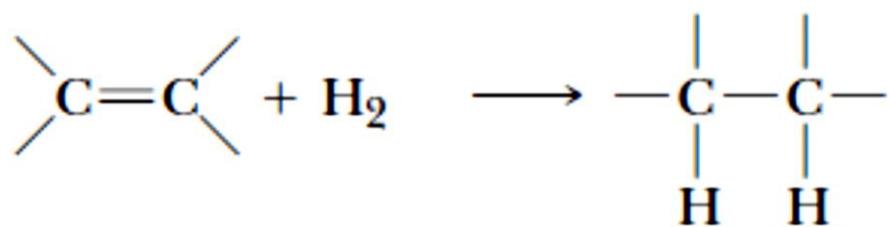
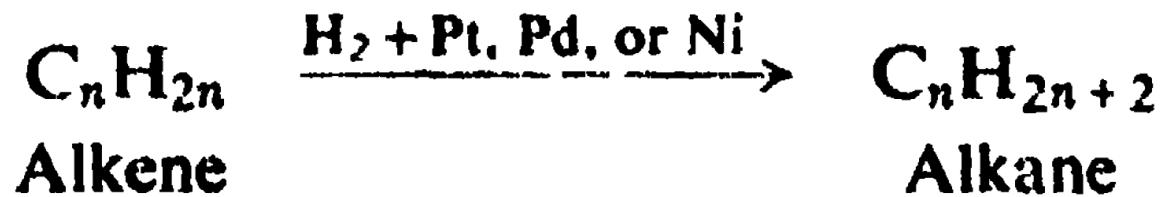


PETROLEUM REFINING PROCESS

2. **Naphthas**, bp 20 to 200 °C, are a mixture of **C5** to **C12** alkanes and cycloalkanes. Naphthas also contain small amounts of aromatic hydrocarbons. The **light naphtha fraction**, bp 20 to 150 °C, is the source of straight-run gasoline and averages approximately 25% of crude petroleum. In a sense, **naphthas** are the most valuable distillation fractions, because they are useful not only as fuel, but also as sources of raw materials for the organic chemical industry.
3. **Kerosene**, bp 175 to 275 °C, is a mixture of **C9** to **C15** hydrocarbons.
4. **Fuel oil**, bp 250 to 400 °C, is a mixture of **C15** to **C18** hydrocarbons. Diesel fuel is obtained from this fraction.
5. **Lubricating oil and heavy fuel oil** distill from the column at temperatures above 350 °C.
6. **Asphalt** is the black, tarry residue remaining after the removal of the other volatile fractions.

PREPARATION OF ALKANES

1. Hydrogenation of alkenes



PREPARATION OF ALKANES

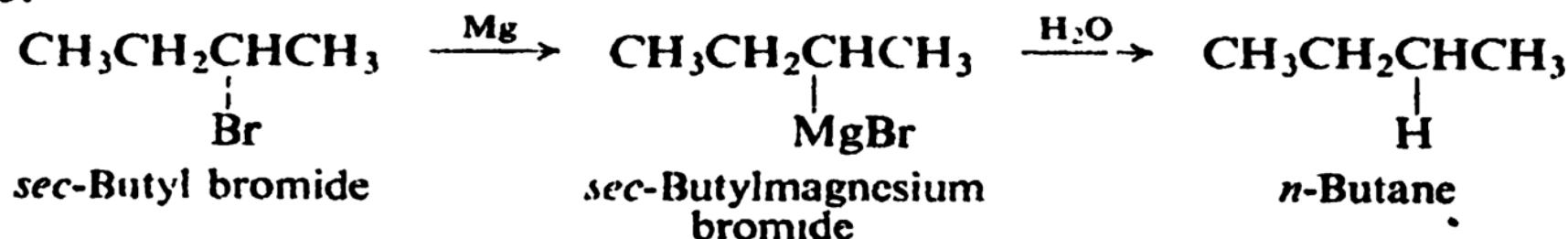
2. Reduction of alkyl halides

(a) Hydrolysis of Grignard reagent:

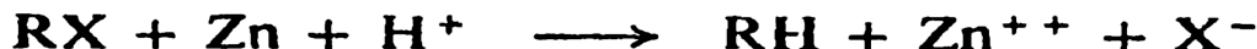
R= any alkyl group



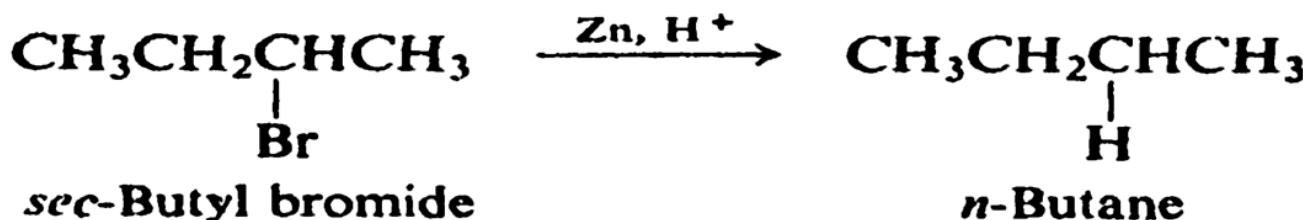
Example:



(b) Reduction by metal and acid:



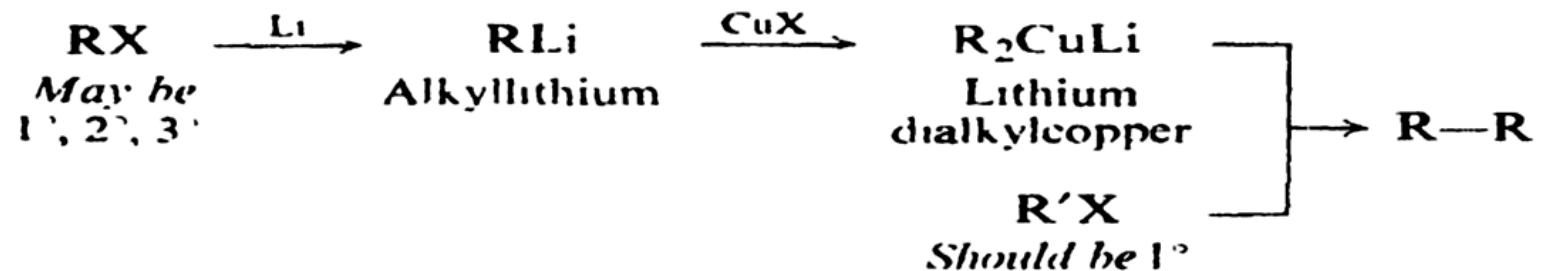
Example:



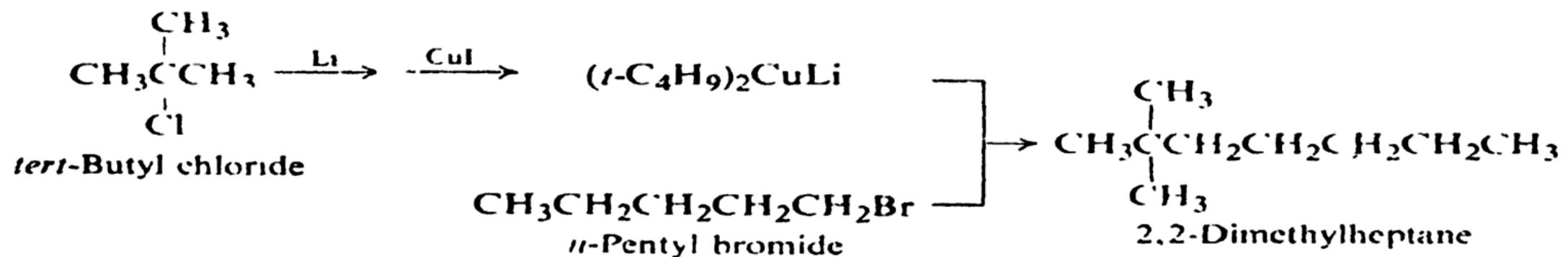
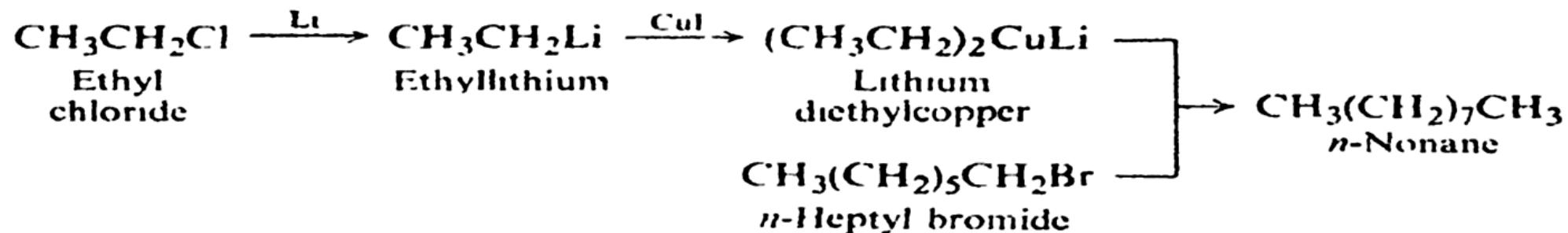
PREPARATION OF ALKANES

3. Coupling of alkyl halides with organometallic compounds

R= any alkyl group

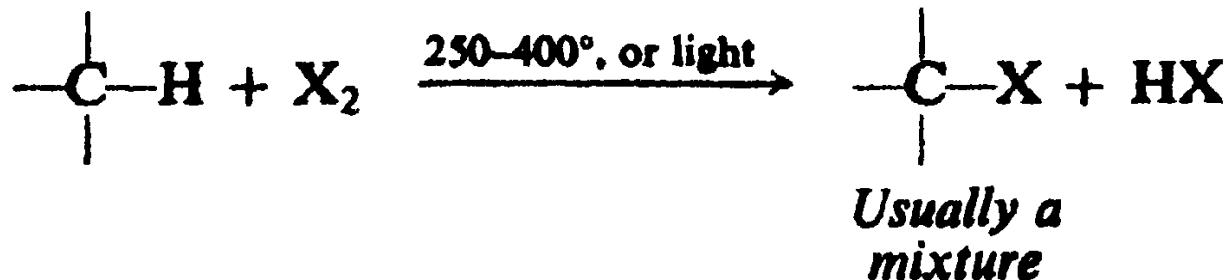


Examples:



REACTIONS OF ALKANES

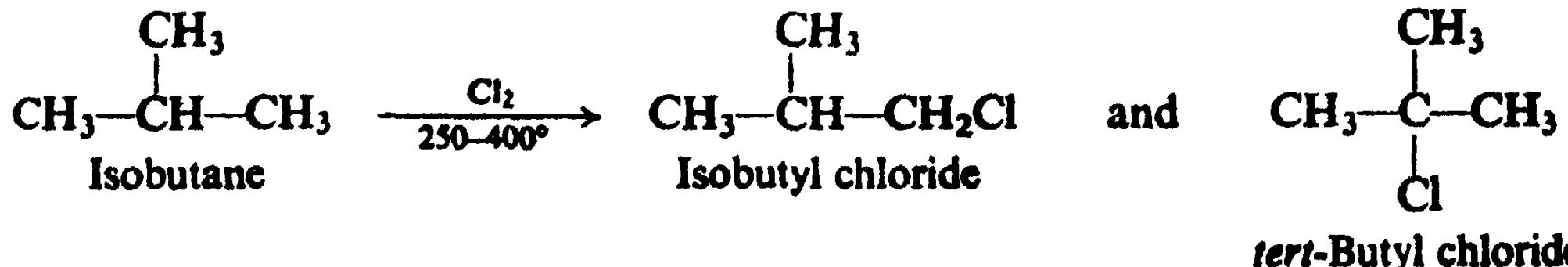
1. Halogenation



Reactivity

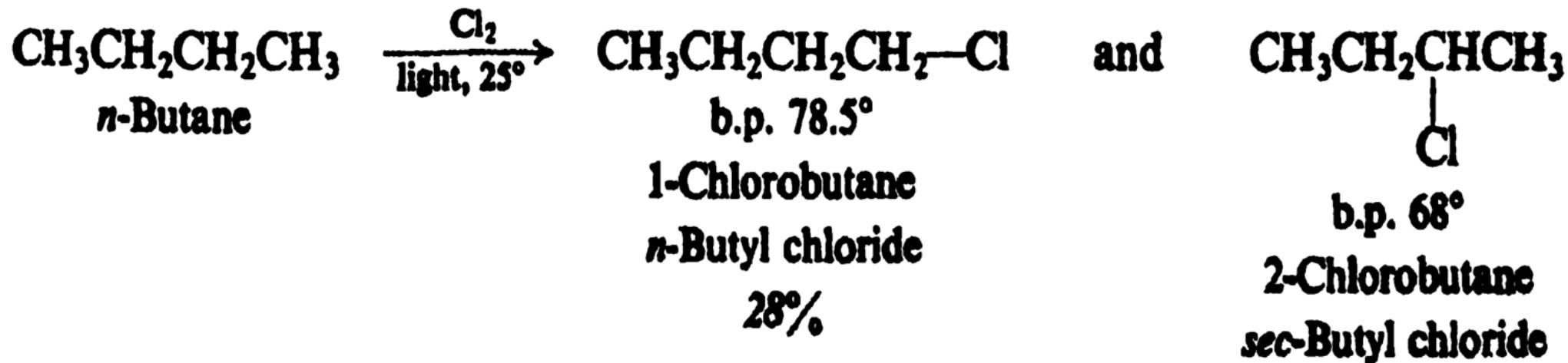
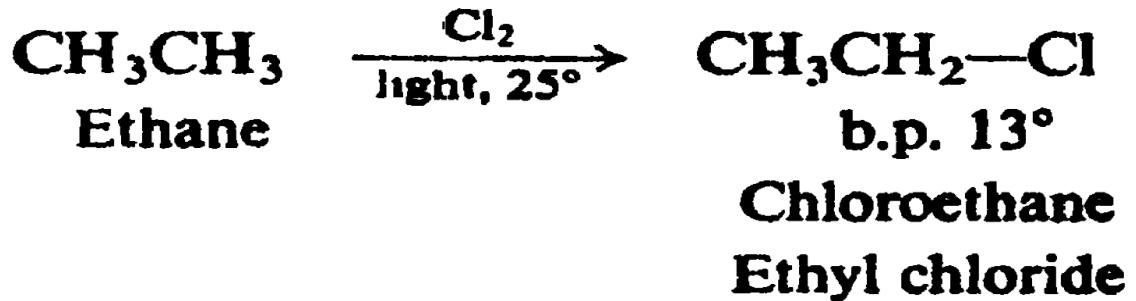


Example:

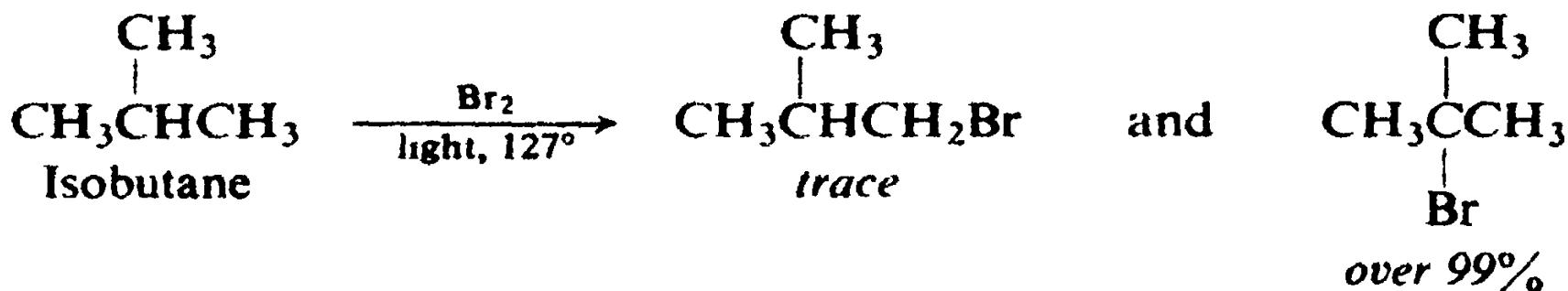
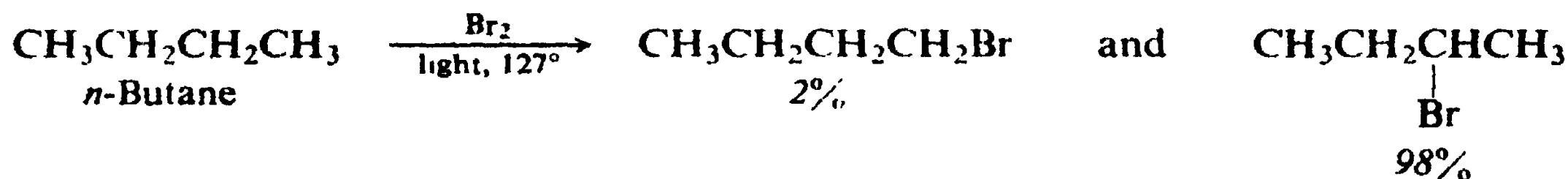
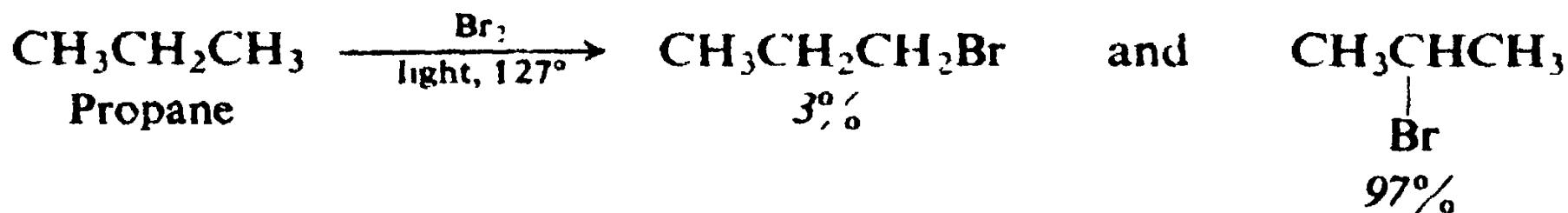
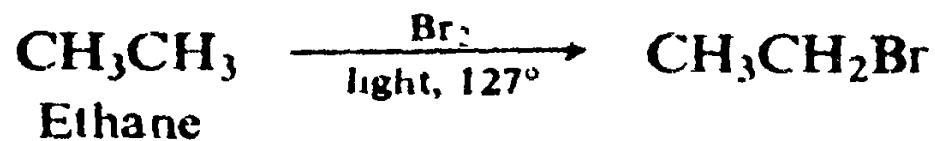


REACTIONS OF ALKANES

1. Halogenation Further Examples:



REACTIONS OF ALKANES: Halogénéation (Examples)



REACTIONS OF ALKANES

2. Combustion

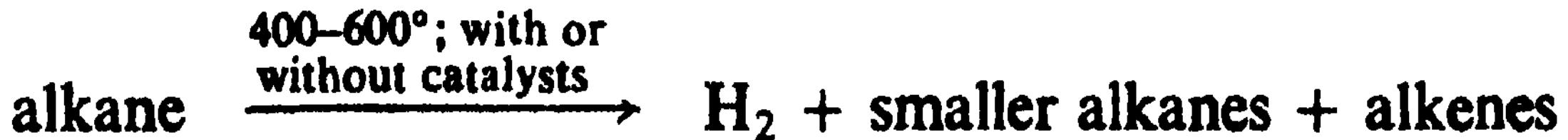


ΔH = heat of combustion

Example:

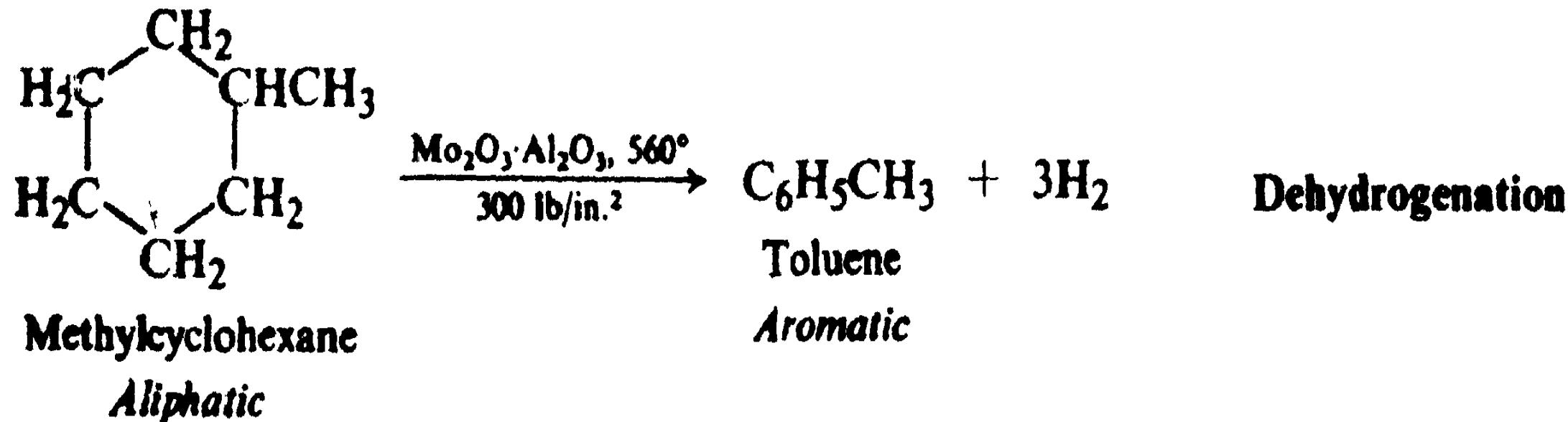


3. Pyrolysis (cracking)



NATURAL SOURCES OF CYCLOALKANES

We have already mentioned that petroleum from certain areas, (in particular California) is rich in cycloalkanes, known to the petroleum industry as **naphthenes**. Among these are cyclohexane, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane. These cycloalkanes are converted by catalytic reforming into aromatic hydrocarbons, and thus provide one of the major sources of these important compounds. For example:



NATURAL SOURCES OF CYCLOALKANES

Human body contains important compounds their structures include cyclic forms. For example:

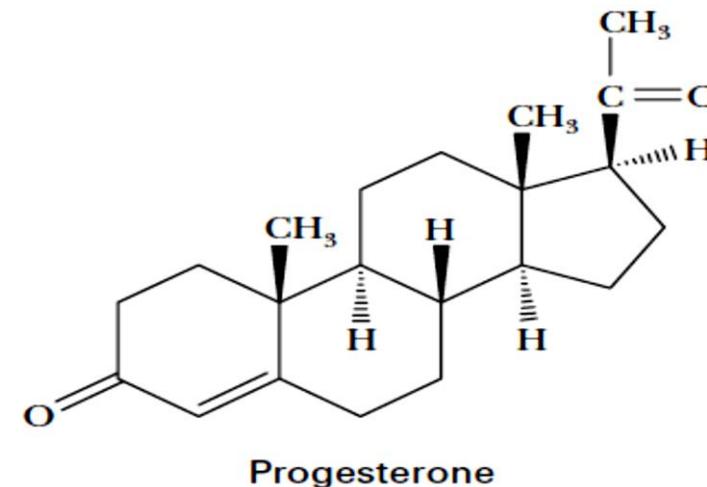
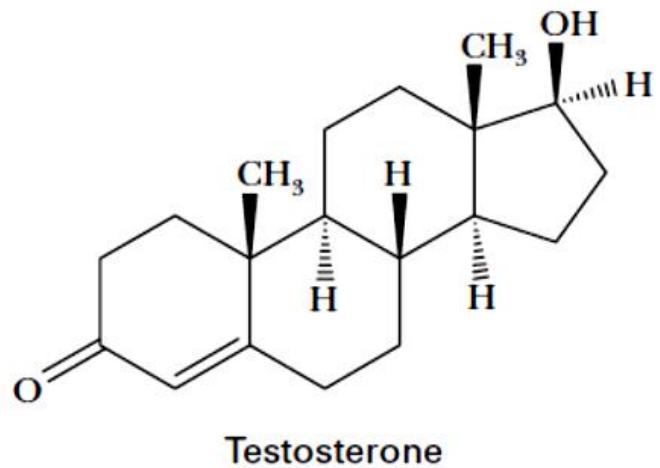
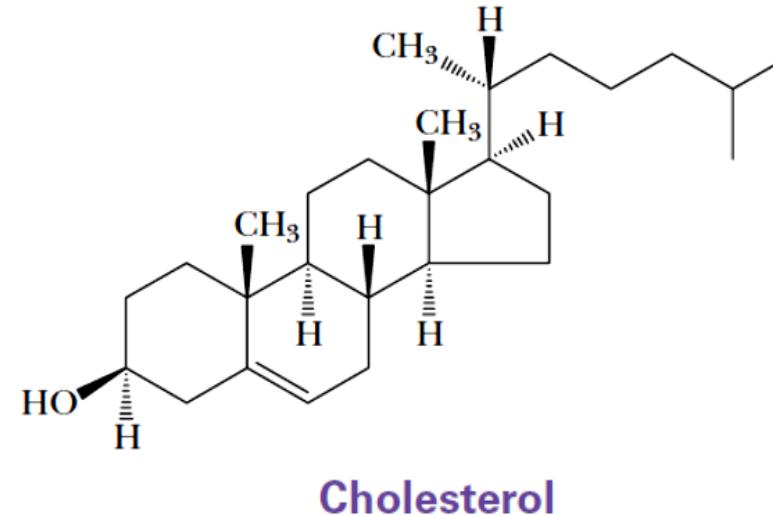
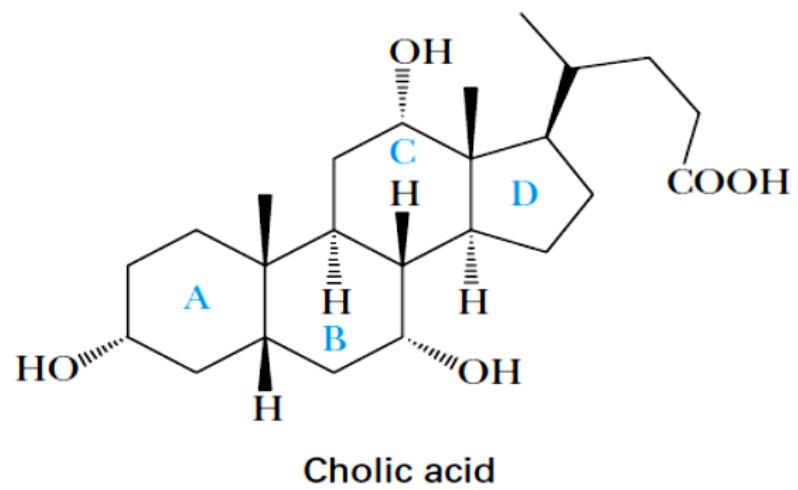
Cholic acid, a component of human bile whose function is to aid in the absorption and digestion of dietary fats.

Cholesterol, a white, water-insoluble, waxy solid found in blood plasma and in all animal tissues, is an integral part of human metabolism.

Testosterone, an androgen (male sex hormones): synthesized in the testes; responsible for development of male secondary sex characteristics.

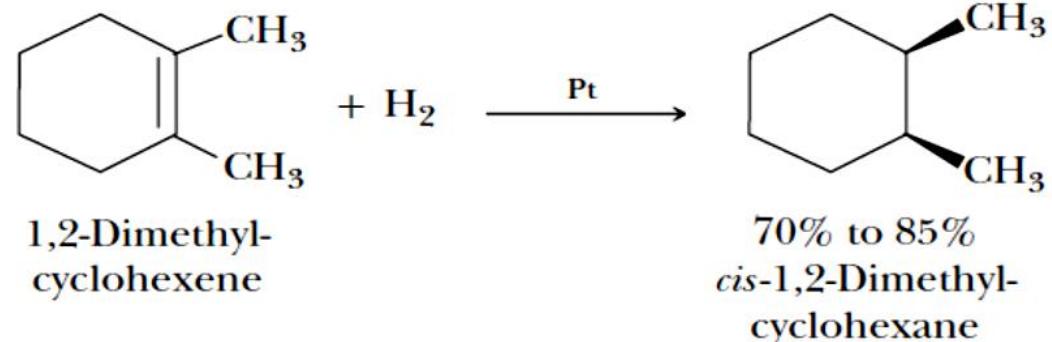
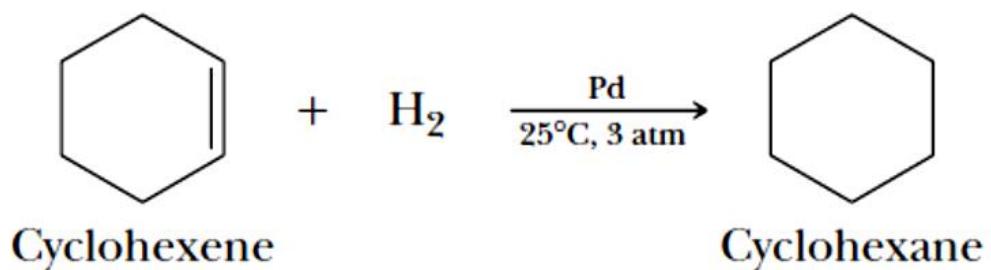
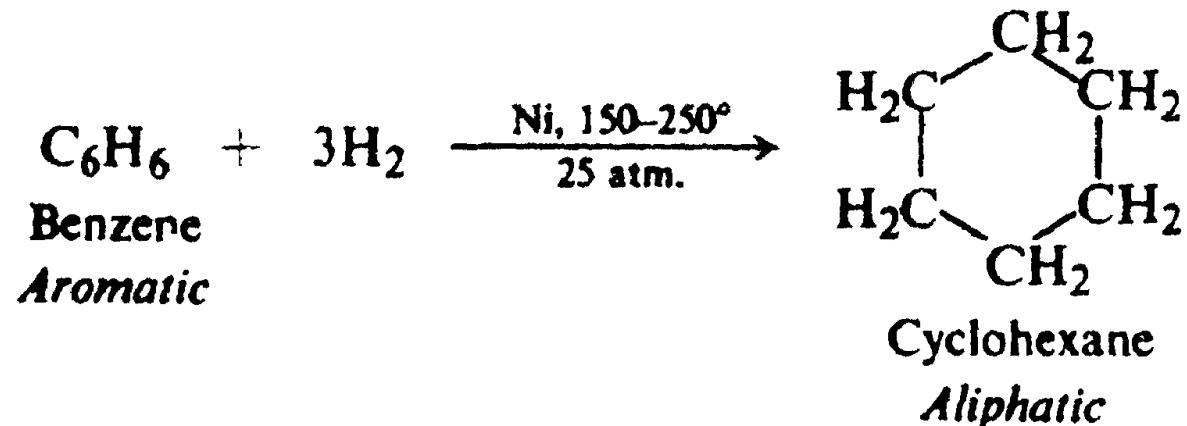
Progesterone, an estrogen (female sex hormones): synthesized in the ovaries; responsible for development of female secondary sex characteristics and control of the menstrual cycle

NATURAL SOURCES OF CYCLOALKANES



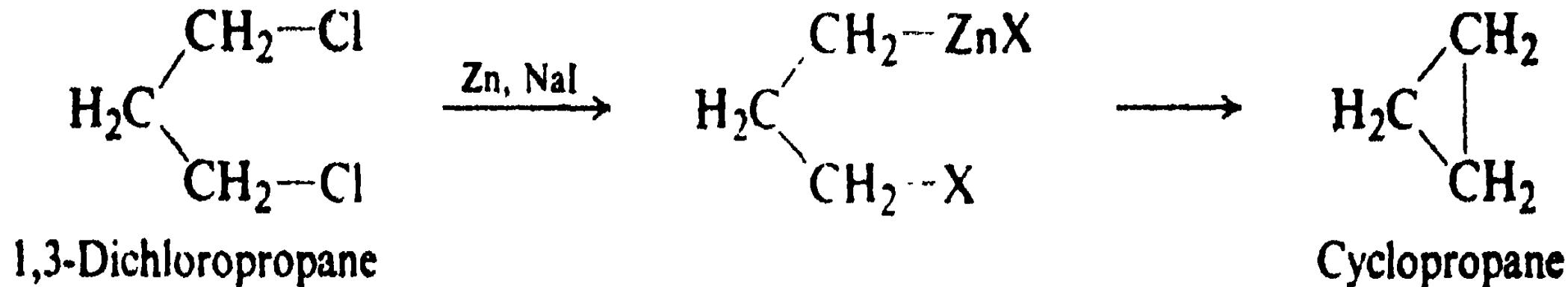
Preparation of Cycloalkanes

1. Hydrogenation of aromatic hydrocarbons or alkenes



Preparation of Cycloalkanes

2. Coupling between two alkyl groups that are part of the same molecule through alkyl dihalide-zinc complex. This particular method is work well only for the preparation of cyclopropane.

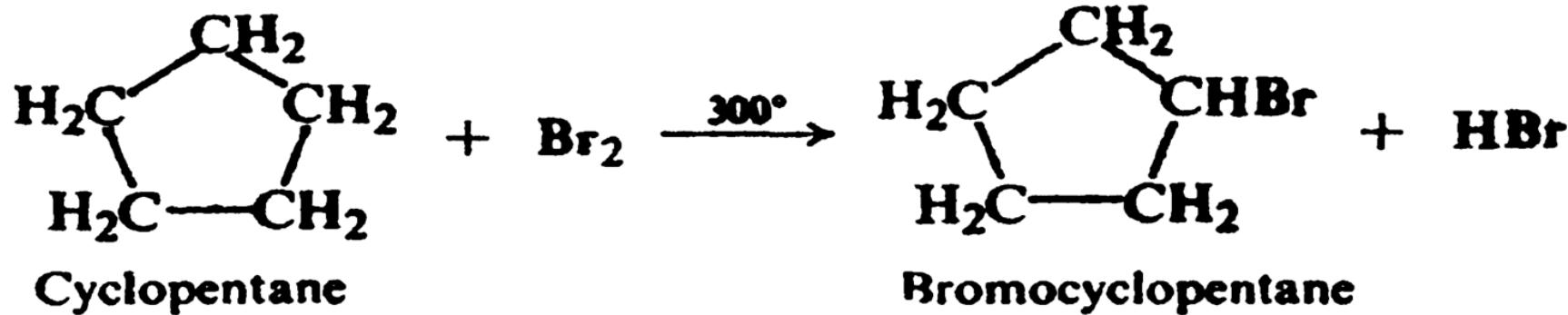
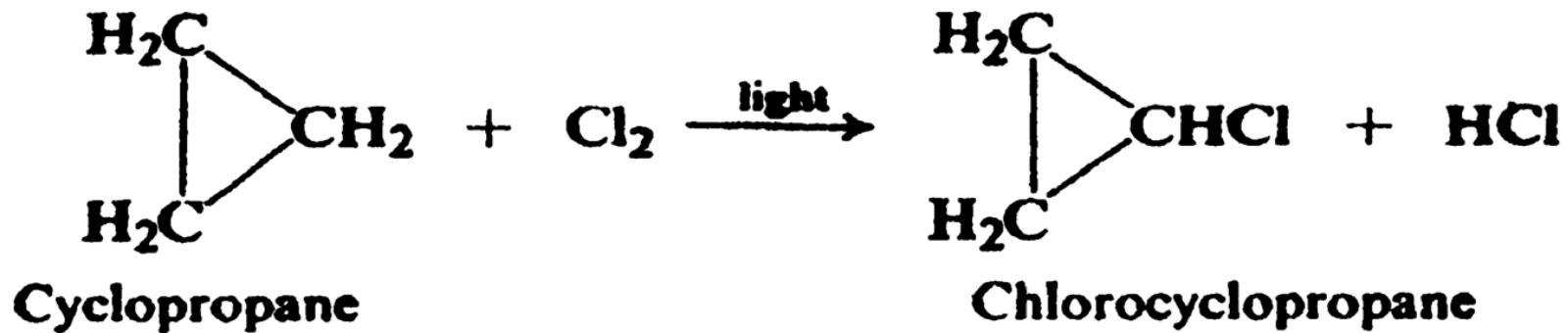


Cycloalkanes are also prepared from other cyclic compounds (e.g., halides or alcohols) by exactly the same methods that are used for preparing open-chain hydrocarbons from other open-chain compounds, as we will see in following chapters.

Reactions of Cycloalkanes

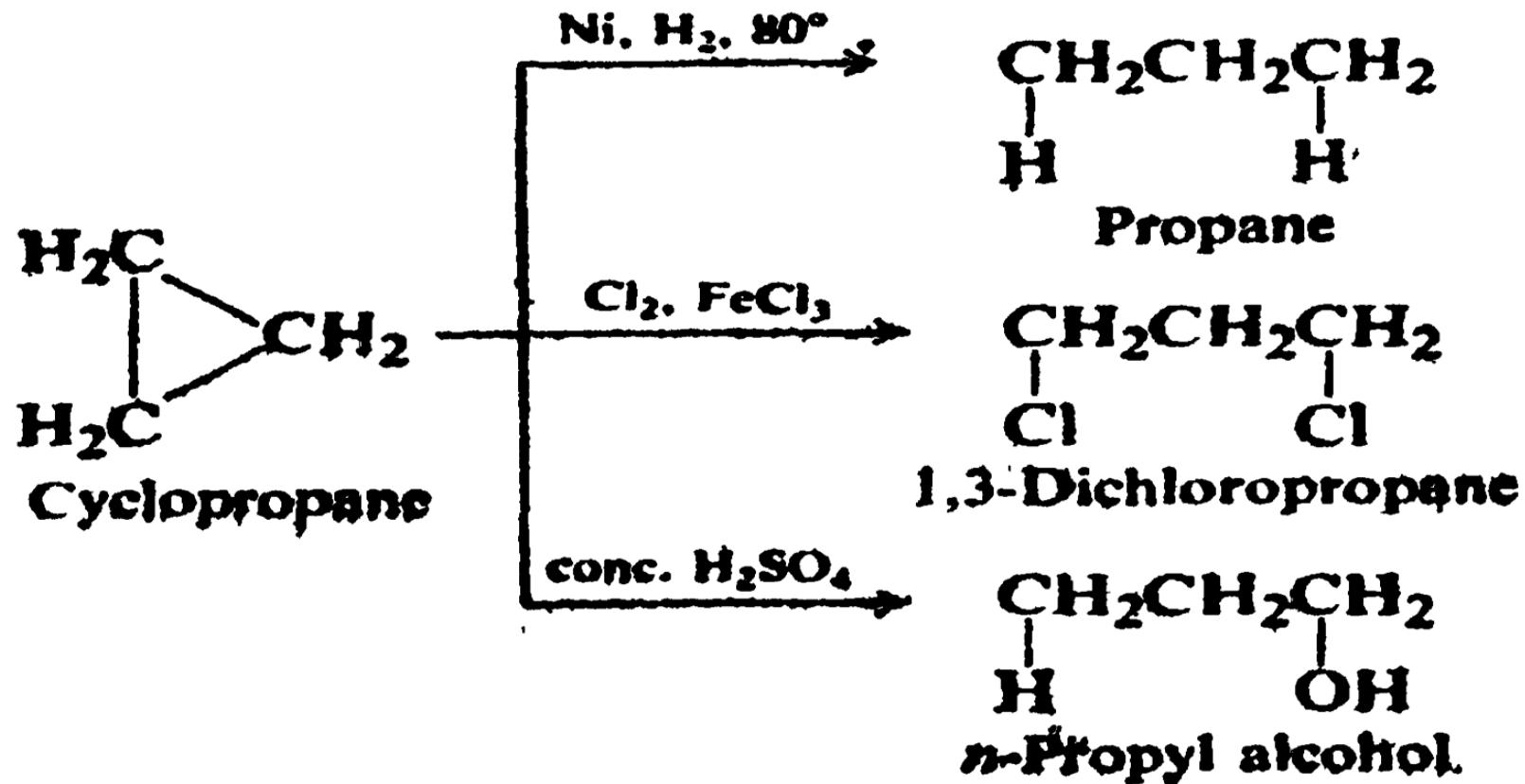
With certain very important and interesting exceptions, cyclic hydrocarbons undergo the same reactions as their open-chain analogs.

1. Halogenation



Reactions of Cycloalkanes

2. Addition reactions: Cyclopropane and cyclobutane undergo certain addition reactions. These addition reactions destroy the cyclopropane and cyclobutane ring systems, and yield open-chain products. For example:



Organic Chemistry for Biology Students

Lecture 3

CHAPTER TWO

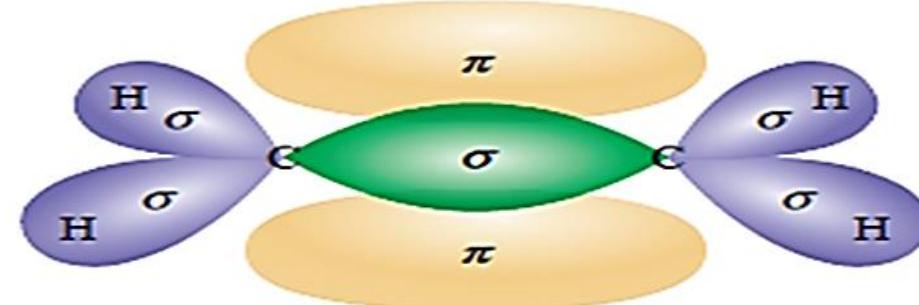
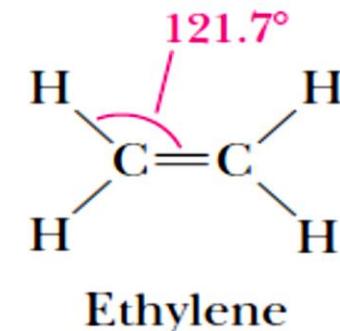
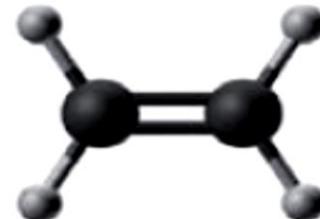
Alkenes *(Structure and preparation)*

Dr. Omar Abdulateef

Structure and Shape of Alkenes

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the **alkenes**, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen. The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process. Since alkenes evidently contain less than the maximum quantity of hydrogen, they are referred to as **unsaturated hydrocarbons**. This unsaturation can be satisfied by reagents other than hydrogen and gives rise to the characteristic chemical properties of alkenes.

The alkenes (also called **olefins**) contain at least one carbon-carbon double bond. Alkenes have the general formula C_nH_{2n} , where $n = 2, 3, \dots$. The simplest alkene is **ethylene** C_2H_4 , in which both carbon atoms are sp^2 -hybridized and the double bond is made up of a strong ***sigma* (σ) bond** and a weak ***pi* (π) bond**.



Geometric Isomers of Alkenes

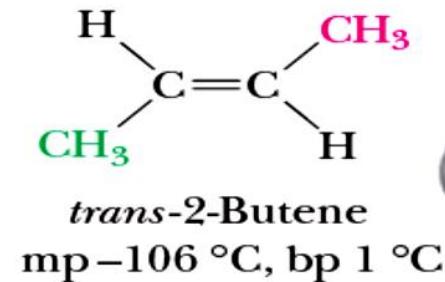
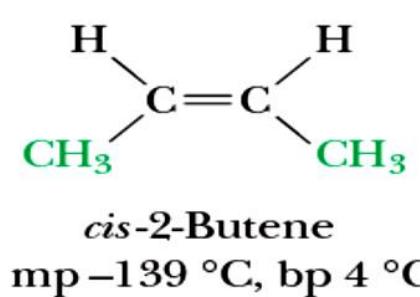
Molecules containing carbon-carbon double bonds (that is, the **alkenes**) may have **geometric isomers**, which have the same type and number of atoms and the same chemical bonds but different spatial arrangements.

cis means that two particular atoms (or groups of atoms) are adjacent to each other.

trans means that the two atoms (or groups of atoms) are across from each other.

Consider, for example, 2-butene: In *cis*-2-butene, the two methyl groups are on the same side of the double bond; in *trans*-2-butene, the two methyl groups are on opposite sides of the double bond.

Cis alkenes are less stable than their *trans* isomers because of nonbonded interaction strain between alkyl substituents on the same side of the double bond in the *cis* isomer, as can be seen in space-filling models of the *cis* and *trans* isomers of 2-butene.



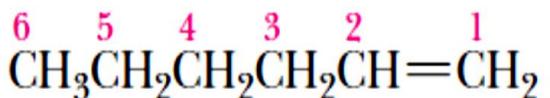
nonbonded interaction (steric) strain makes *cis*-2-butene less stable than *trans*-2-butene

Nomenclature of Alkenes

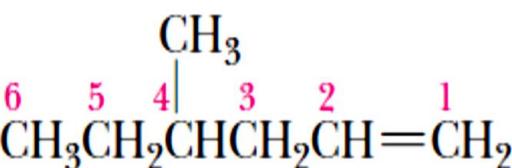
The IUPAC System Rules

1. Number the longest carbon chain that contains the double bond in the direction that gives the carbon atoms of the double bond the lower set of numbers.
 2. Use the number of the first carbon of the double bond to show its location.
 3. Name branched or substituted alkenes in a manner similar to the way we name alkanes
 4. Name the main (parent) chain by changing the **-an-** infix of the parent alkane to **-en-**

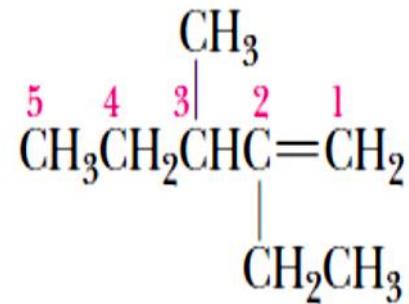
[نتبع نفس قواعد تسمية الالكانات و يراعى عند ترقيم السلسة الأطولة ان تأخذ الاصرة المزدوجة اصغر الأرقام ويستبدل المقطع (-an) في نهاية اسم الالكان **بالمقطع (-en)** . ويجب تحديد نوع الايزومير الهندسي هل هو *cis* او *trans* لجزئية الالكين]



1-Hexene



4Methyl-1-hexene

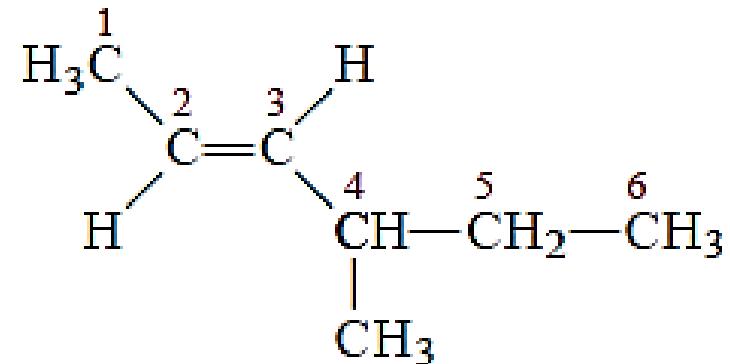
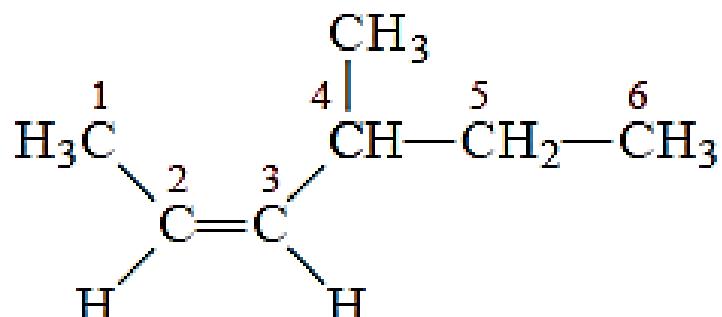
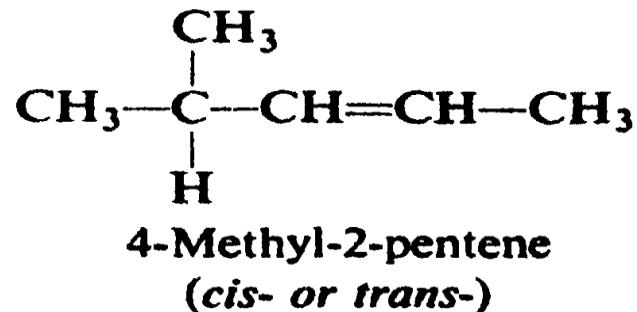
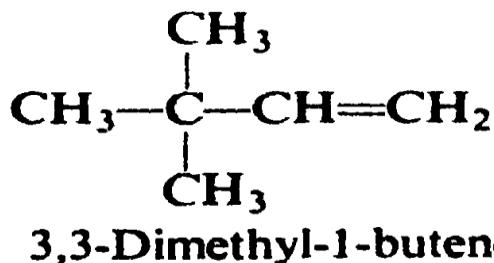
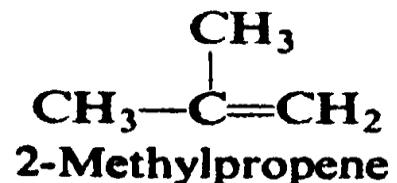


2-Ethyl-3-methyl-1-pentene

in naming alkenes, the parent chain is the longest chain containing the entire C=C bond, even if a different chain that doesn't contain the C=C bond is longer

Nomenclature of Alkenes

Examples:



cis-4-methyl-2-hexene

trans-4-methyl-2-hexene

Nomenclature of Alkenes

Problem: (1) Give the structural formula of:

(a) 3,6-dimethyl-1-octene

(b) 3-chloropropene

(c) 2,4,4-trimethyl-2-pentene

(d) *trans*-3,4-dimethyl-3-hexene

(e) 2,3-dimethyl-2-butene

(f) 3-bromo2-methylpropene

(2) Draw out the structural formula and give the IUPAC name of:

(a) *cis*-CH₃CH₂CH=CHCH₂CH₃

(b) *trans*-(CH₃)₂CHCH=CHCH(CH₃)₂

Industrial source of Alkenes

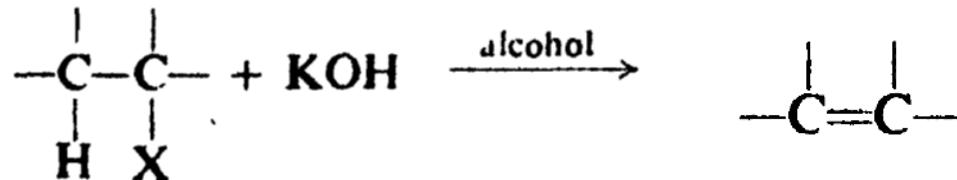
Alkenes are obtained in industrial quantities chiefly by the cracking of petroleum. The smaller alkenes can be obtained in pure form by fractional distillation and are thus available for conversion into a large number of important aliphatic compounds. Higher alkenes, which cannot be separated from the complicated cracking mixture, remain as valuable components of gasoline.

Physical Properties of Alkenes

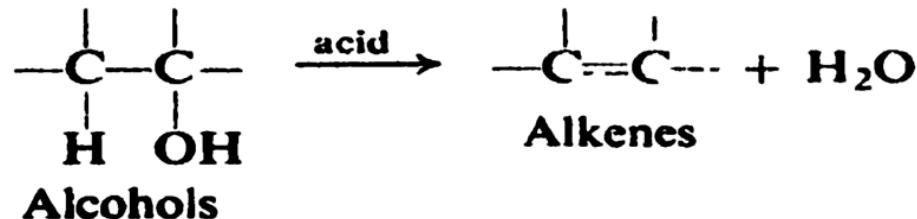
Alkenes are nonpolar compounds, and the only attractive forces between their molecules are dispersion forces. Therefore, their physical properties are similar to those of alkanes with the same carbon skeletons. Alkenes that are liquid at room temperature have densities less than 1.0 g/mL . Thus, they are less dense than water. Like alkanes, alkenes and alkynes are nonpolar and are soluble in each other. Because of their contrasting polarity with water, they do not dissolve in water. Instead, they form two layers when mixed with water or another polar organic liquid such as ethanol.

PREPARATION OF ALKENES

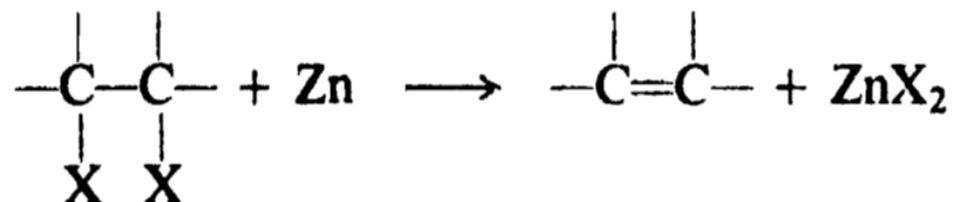
1. Dehydrohalogenation of alkyl halides: (Elimination of HX)



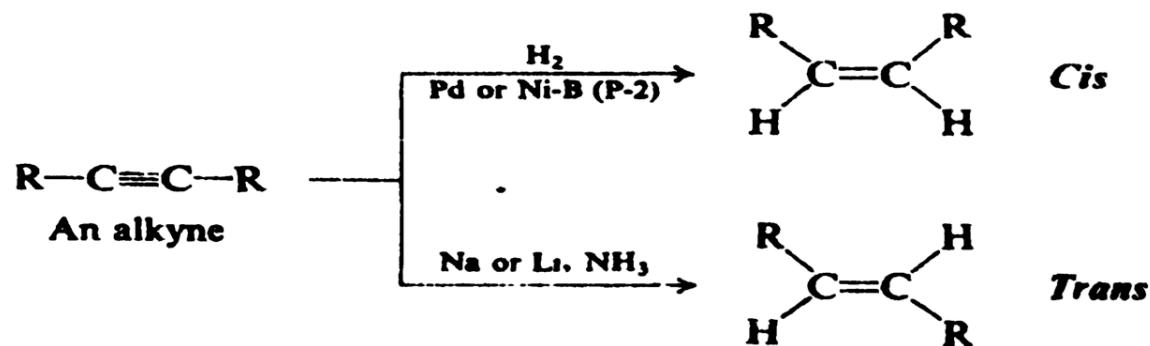
2. Dehydration of alcohols: (Elimination of H₂O)



3. Dehalogenation of vicinal dihalides

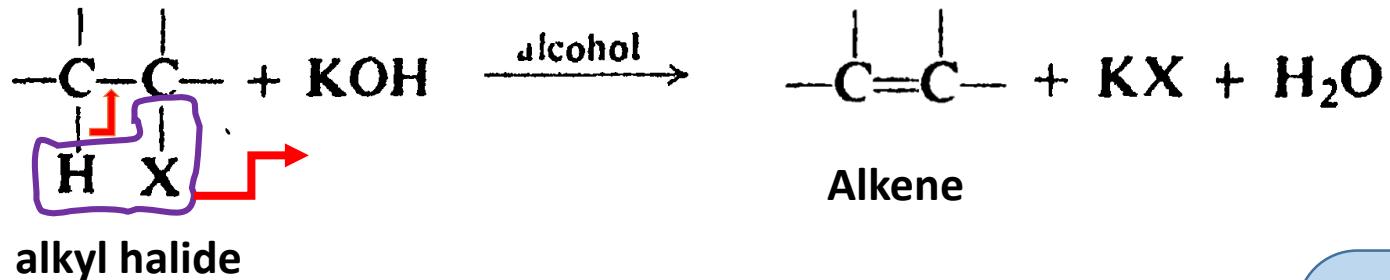


4. Reduction of alkynes

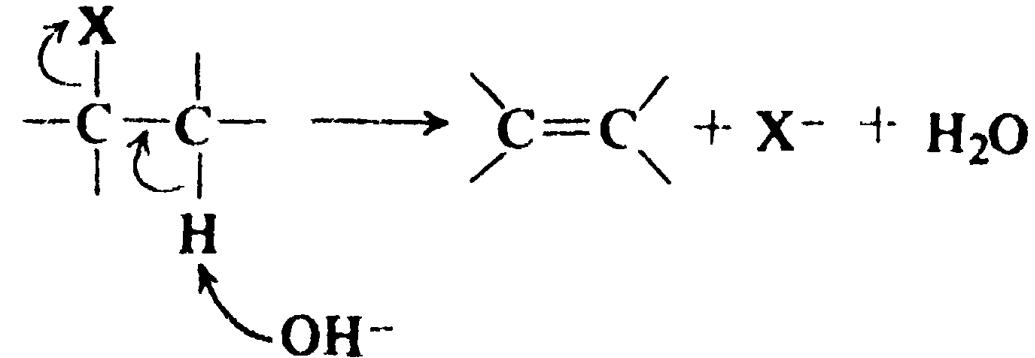


PREPARATION OF ALKENES

1. Dehydrohalogenation of alkyl halides: (*Elimination of HX*)



Ease of dehydrohalogenation of alkyl halides

$$3^\circ > 2^\circ > 1^\circ$$


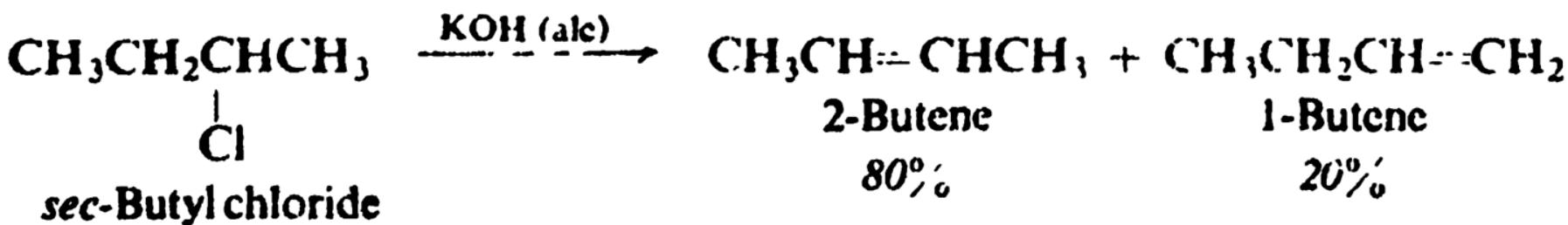
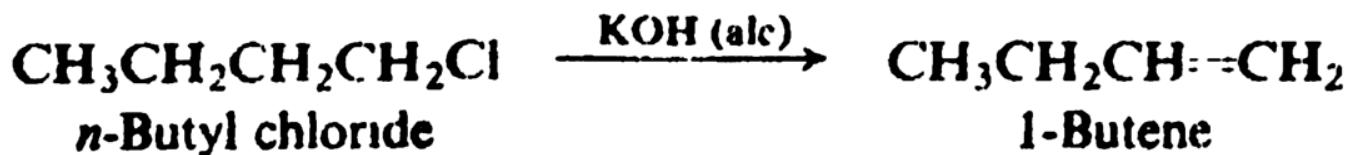
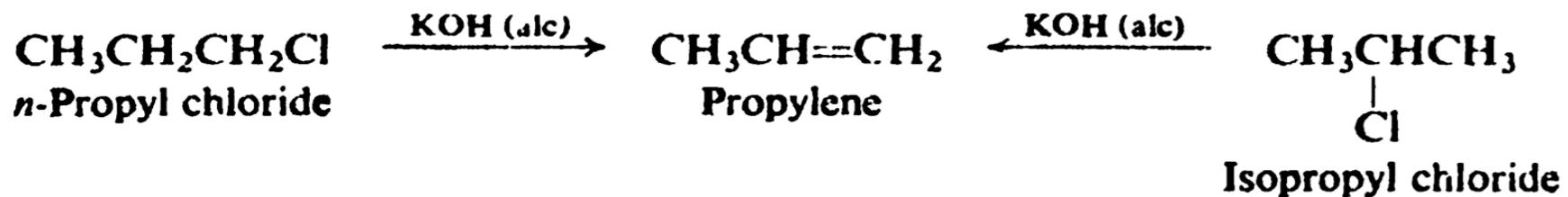
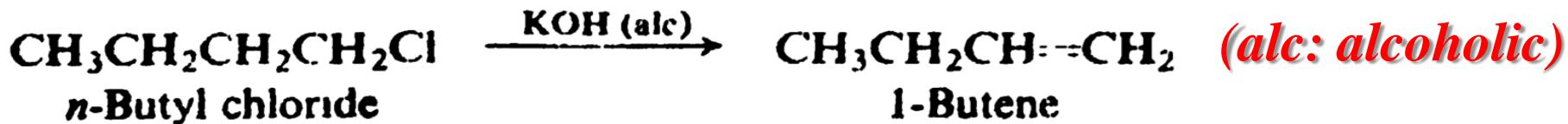
where arrows show the direction of electron shift

The function of hydroxide ion is to pull a hydrogen ion away from carbon; simultaneously a halide ion separates and the double bond forms

The breaking of the C–H and C–X bonds occurs in an unsymmetrical fashion: hydrogen relinquishes both electrons to carbon, and halogen retains both electrons. The electrons left behind by hydrogen are now available for formation of the second bond (the π bond) between the carbon atoms

PREPARATION OF ALKENES: (Dehydrohalogenation of alkyl halides)

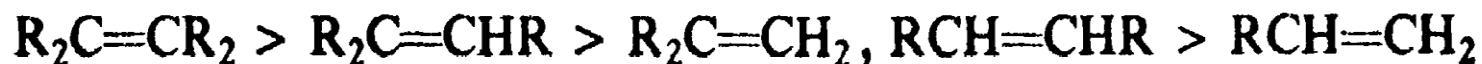
Examples:



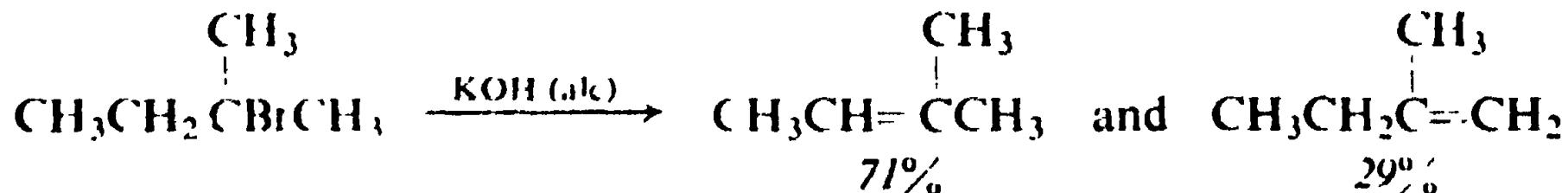
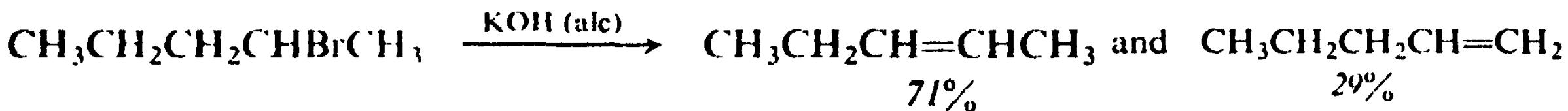
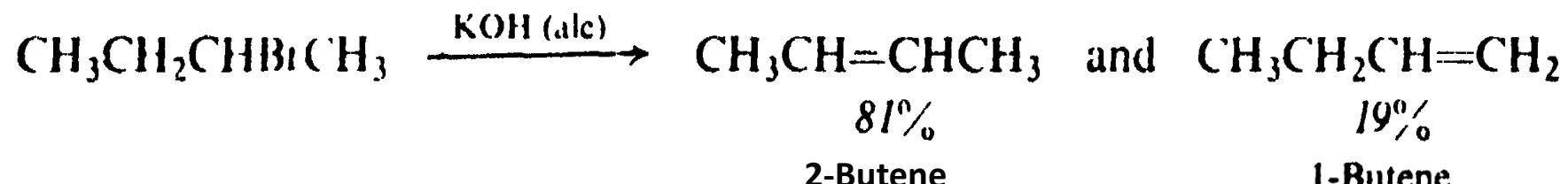
PREPARATION OF ALKENES

Orientation and reactivity in dehydrohalogenation

In dehydrohalogenation, **the more stable the alkene the more easily it is formed**



Ease of formation of alkenes (Stability of alkenes)



In cases where a mixture of isomeric alkenes can be formed, **the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly-bonded carbon atoms.**

PREPARATION OF ALKENES

Problem (2.1): Give structures of all alkenes expected from dehydrohalogenation of the following alkyl halides and predict the major product of each reaction:

(a) 1-chloropentane

(b) 2-bromopentane

(c) 3-chloropentane

(d) 2-chloro-2-methylbutane

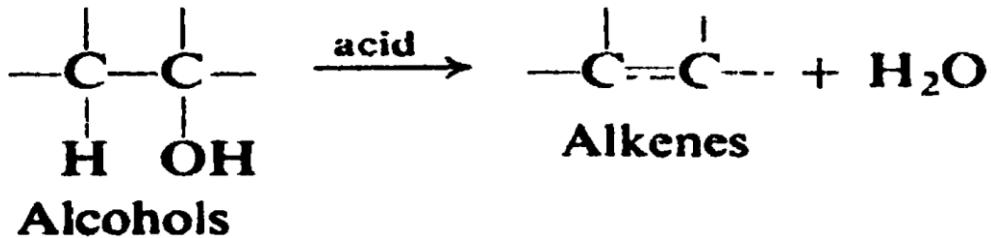
(e) 3-bromo-2-methylbutane

(f) 2-chloro-2,3-dimethylbutane

(g) 1-bromo-2,2-dimethylpropane.

PREPARATION OF ALKENES

2. Dehydration of alcohols: (Elimination of H₂O)



Ease of dehydration of alcohols

$3^\circ > 2^\circ > 1^\circ$

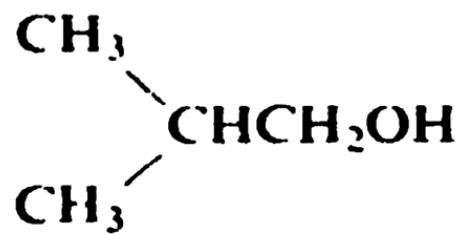


Alcohols are compounds of the general formula, ROH, where R is any alkyl group: the hydroxyl group, -OH, is characteristic of alcohols, just as the C-C double bond is characteristic of alkenes. An alcohol is commonly named by naming the alkyl group that holds the hydroxyl group and following this by the word alcohol. It is classified as primary (1°), secondary (2°), or tertiary (3°), depending upon the nature of the carbon atom holding the hydroxyl group. For example:



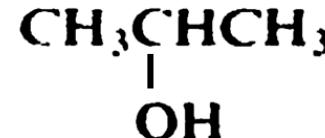
Ethyl alcohol

A primary alcohol



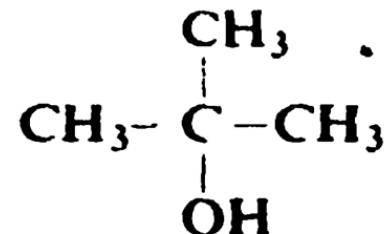
Isobutyl alcohol

A primary alcohol



Isopropyl alcohol

A secondary alcohol



tert-Butyl alcohol

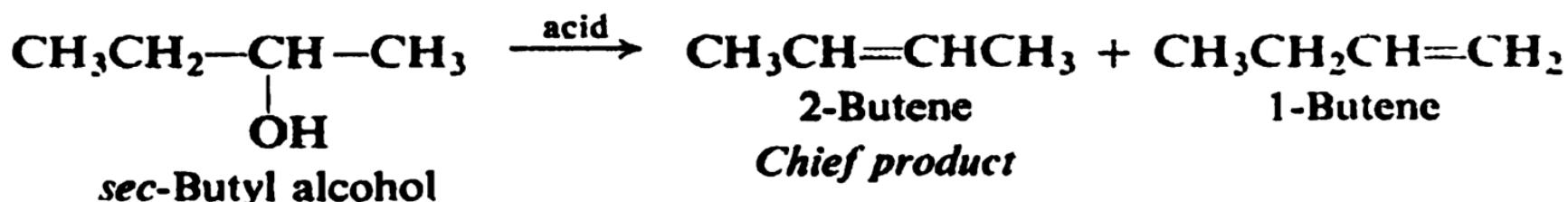
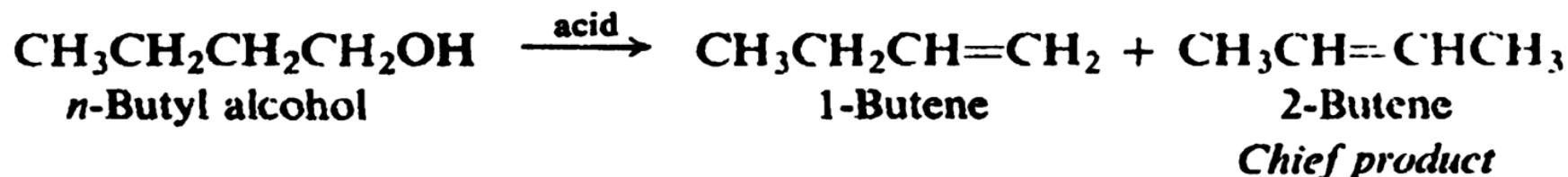
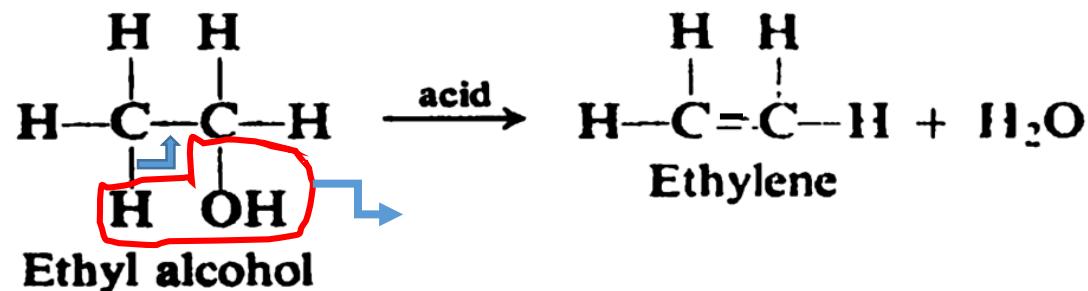
A tertiary alcohol

PREPARATION OF ALKENES

2. Dehydration of alcohols

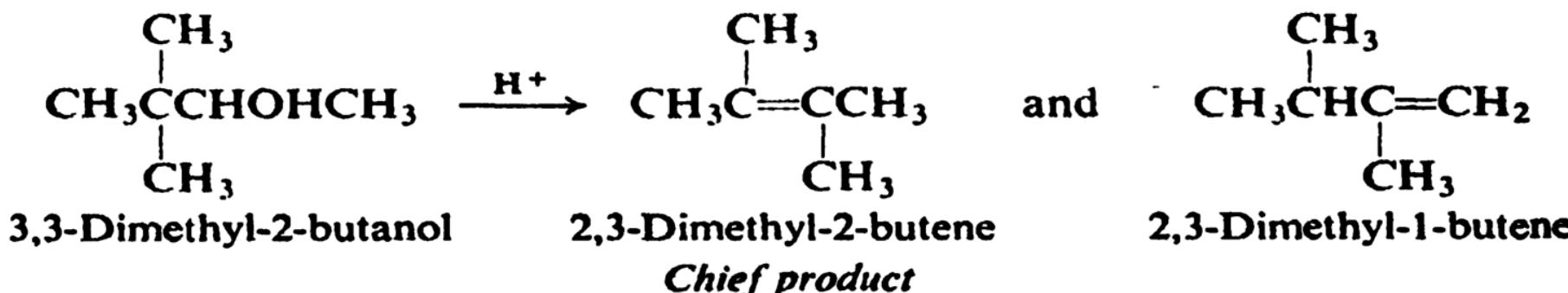
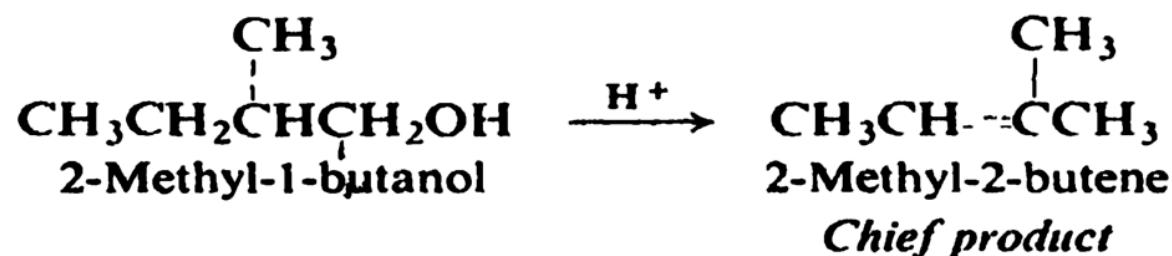
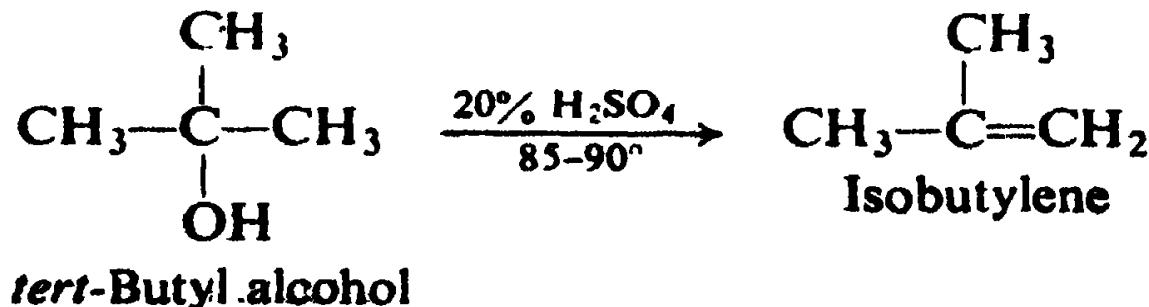
An alcohol is converted into an alkene by **dehydration**: elimination of a molecule of water. Dehydration requires the presence of an **acid** and the application of **heat**.

Examples:



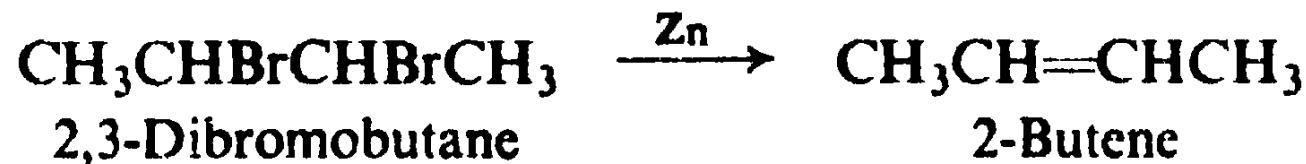
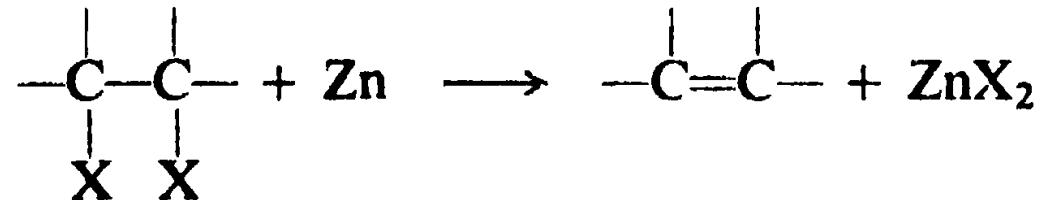
PREPARATION OF ALKENES

2. Dehydration of alcohols

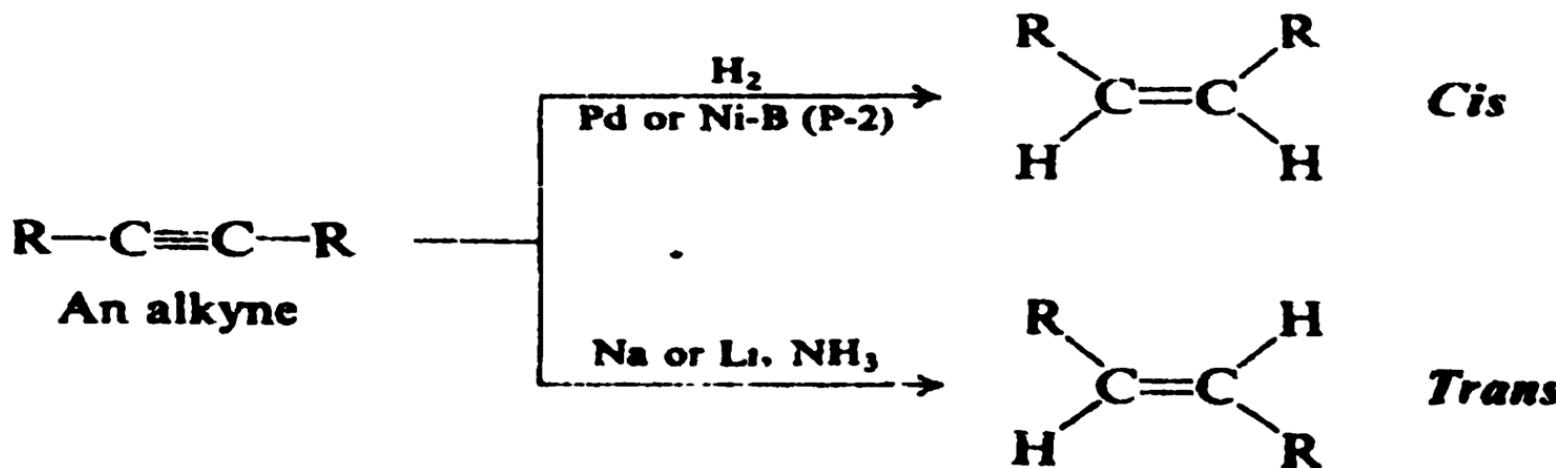


PREPARATION OF ALKENES

3. Dehalogenation of vicinal dihalides



4. Reduction of alkynes



Organic Chemistry for Biology Students

Lecture 4

CHAPTER TWO

Alkenes *(Reactions of Alkenes)*

Dr. Omar Abdulateef

The functional group

Over 10 million organic compounds have been discovered or made by organic chemists! Surely it would seem to be an almost impossible task to learn the physical and chemical properties of this many compounds. While organic compounds can undergo a wide variety of chemical reactions, only certain portions of their structure are changed in any particular reaction.

*The atom or group of atoms that defines the structure of a particular family of organic compounds and, at the same time, determines their properties is called **the functional group**.*

In alkyl halides the functional group is the halogen atom, and in alcohols the –OH group; **in alkenes it is the carbon- carbon double bond.**

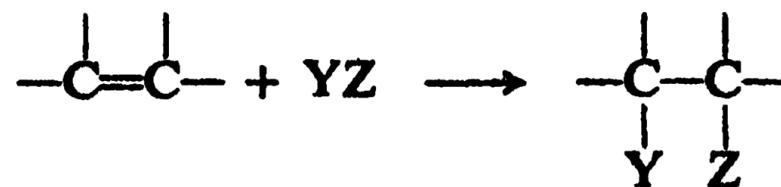
The reactions that are characteristic of each of these compounds are those that occur at the halogen atom or the hydroxyl group or the carbon-carbon double bond. **Functional group**, therefore, *is the part of an organic molecule that undergo chemical reactions.*

The characteristic feature of the alkene structure is the **carbon-carbon double bond**. The characteristic reactions of an alkene are those that take place at the double bond.

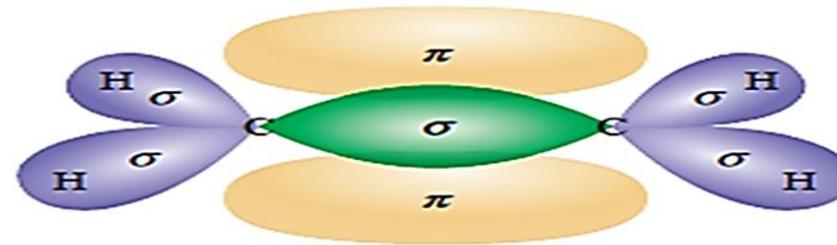
Therefore, you do not have to study the chemical reactions of even a fraction of the 10 million known organic compounds. Instead you need only to identify a few characteristic types of functional groups and then study the chemical reactions that each undergoes.

Reactions of the carbon-carbon double bond: ADDITION REACTIONS

The double bond consists of a strong σ bond and a weak π bond; we might expect, therefore, that reaction would involve the breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort, where *the π bond is broken and two strong σ bonds are formed in its place.*



Addition



A reaction in which two molecules combine to yield a single molecule of product is called an **addition reaction**. In contrast, substitution reaction where part of the reagent is substituted for a portion of the organic molecule.

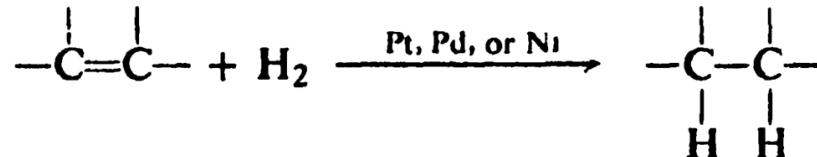
In our structure of the bond there is a cloud of π electrons above and below the plane of the atoms. These loosely held π electrons are particularly available to a **reagent** that is **seeking electrons**.

It is not surprising, then, that in many of its reactions the carbon-carbon double bond serves as a **source of electrons**.

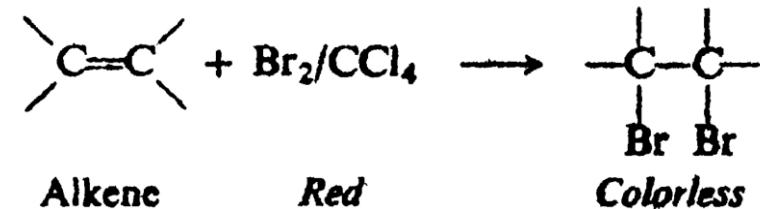
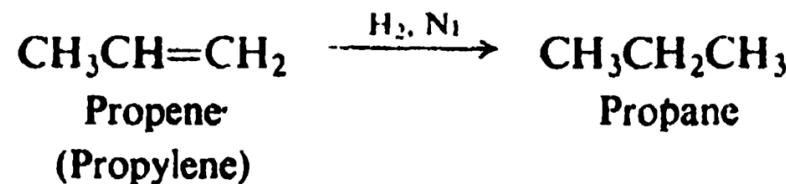
The reagents that are seeking a pair of electrons are called **electrophilic reagents** (Greek: electron-loving). The typical reaction of an alkene is **electrophilic addition**.

Reactions of the carbon-carbon double bond: ADDITION REACTIONS

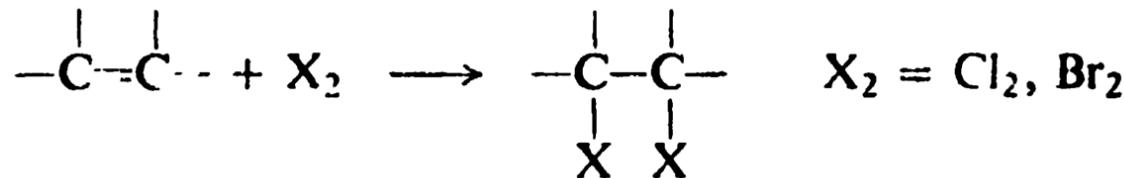
1. Addition of hydrogen. (Catalytic hydrogenation)



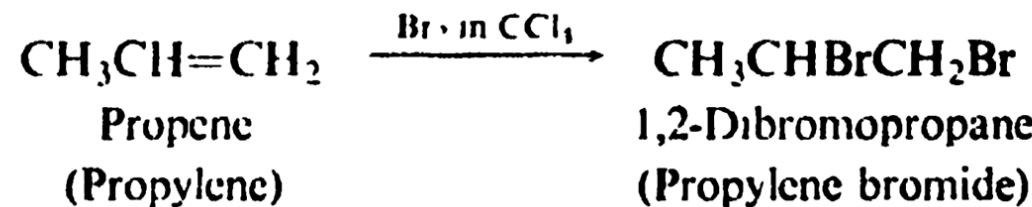
Example:



2. Addition of halogens



Example:

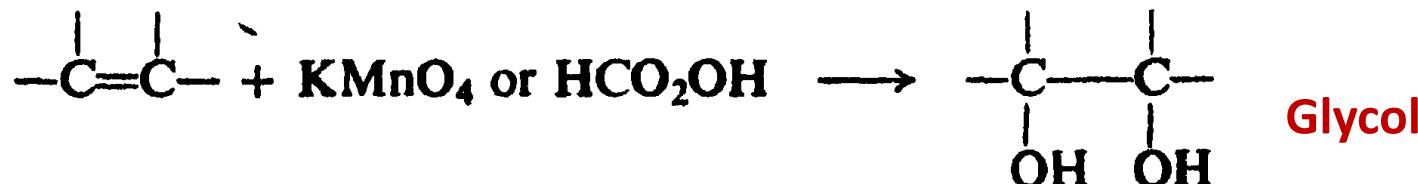


A solution of Br_2 in CCl_4 is red. Add a few drops of an alkene and the red color disappears.

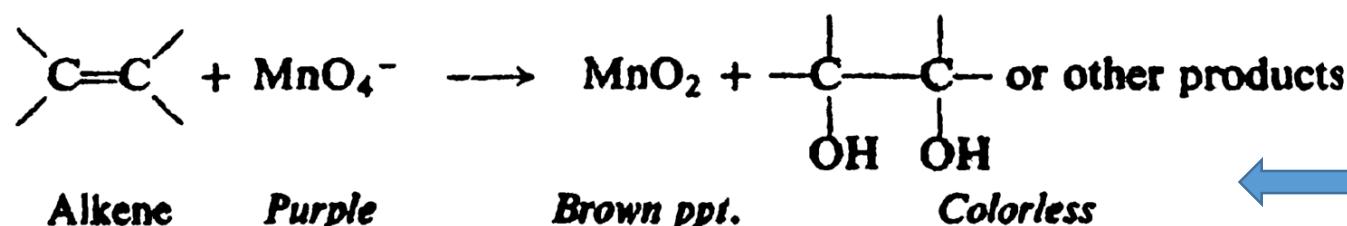
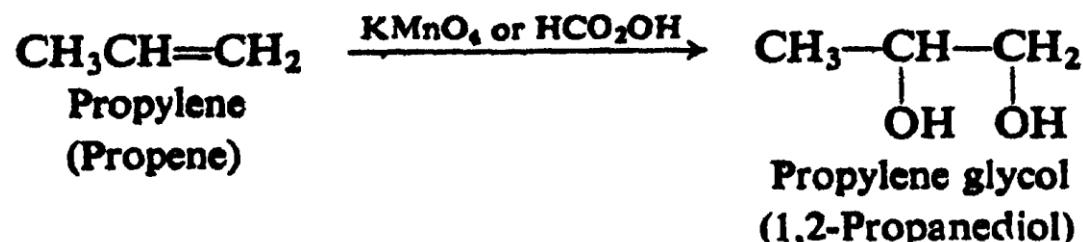
Reactions of the carbon-carbon double bond: ADDITION REACTIONS

3. Hydroxylation. Glycol formation

Certain oxidizing agents convert alkenes into compounds known as **glycols**. Glycols are simply dihydroxy alcohols. Of the numerous oxidizing agents that cause hydroxylation, two of the most commonly used are (a) cold alkaline **KMnO₄**, and (b) peroxyformic acid **HCO₂OH**.



Example:

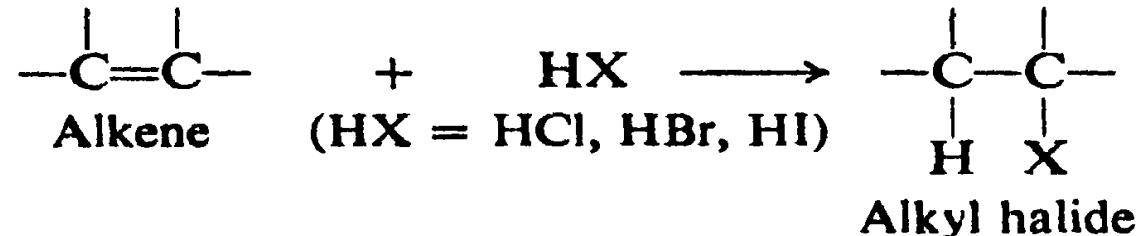


Oxidation by permanganate is the basis of a very useful qualitative analytical test for alkenes known as the **Baeyer test**. Purple color of permanganate MnO_4^- disappears and is replaced by brown MnO_2 precipitate.

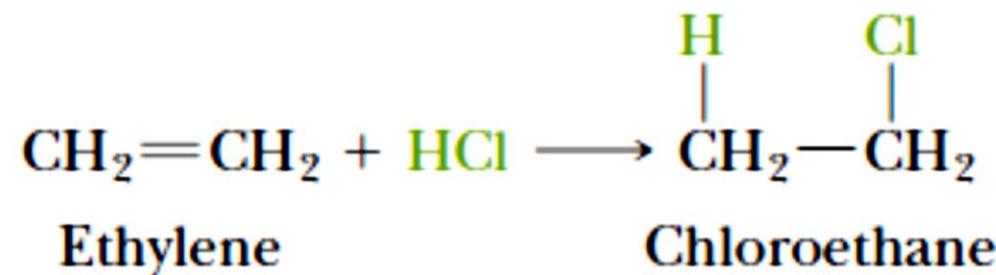
Reactions of the carbon-carbon double bond: ADDITION REACTIONS

4. Addition of hydrogen halides. (Markovnikov's rule)

The hydrogen halides HCl, HBr, and HI add to alkenes to give alkyl halides.



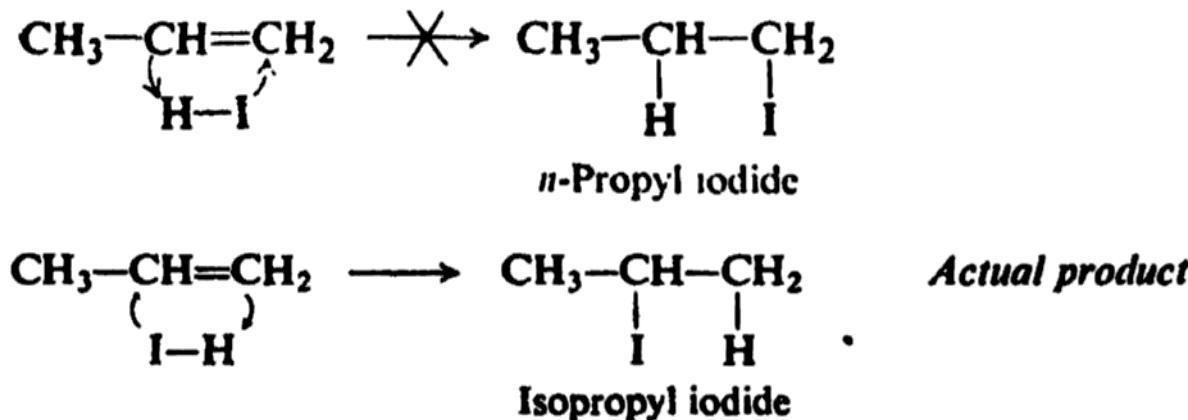
In this way, the addition of HCl to ethylene gives chloroethane:



Reactions of the carbon-carbon double bond: ADDITION REACTIONS

Addition of hydrogen halides. (Markovnikov's rule)

Propene could yield either of two products, the n-propyl halide or the isopropyl halide, depending upon the orientation of addition, that is, depending upon which carbon atoms the hydrogen and halogen become attached to. Actually, it is found that the isopropyl halide greatly predominates.

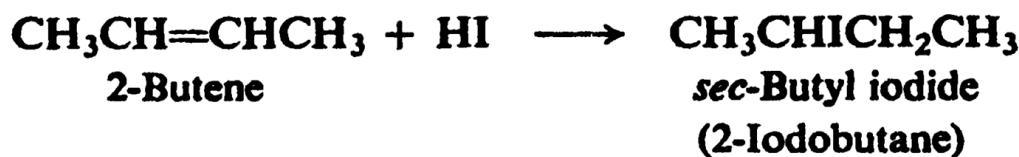
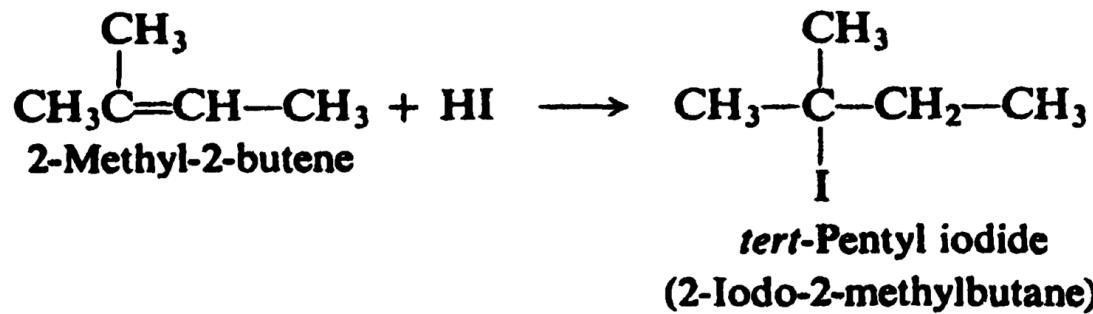
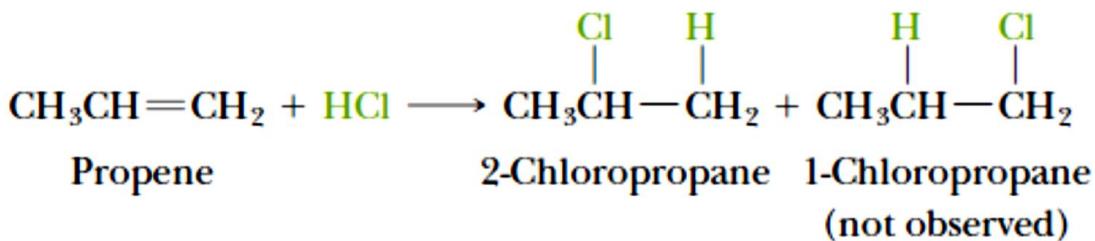


Examination of a large number of such additions showed the Russian chemist Vladimir Markovnikov (of the University of Kazan) that where two isomeric products are possible, one product usually predominates. He pointed out in 1869 that the orientation of addition follows a pattern which we can summarize as: *In the ionic addition of an acid to the carbon-carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon atom that already holds the greater number of hydrogens.* This statement is generally known as Markovnikov's rule.

Reactions of the carbon-carbon double bond: ADDITION REACTIONS

Addition of hydrogen halides. (Markovnikov's rule)

Examples:

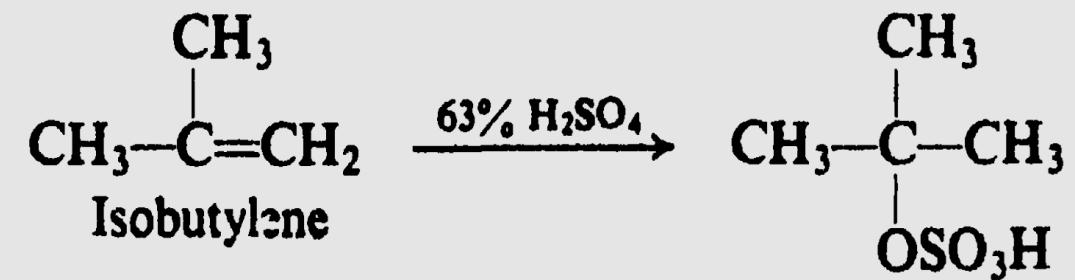
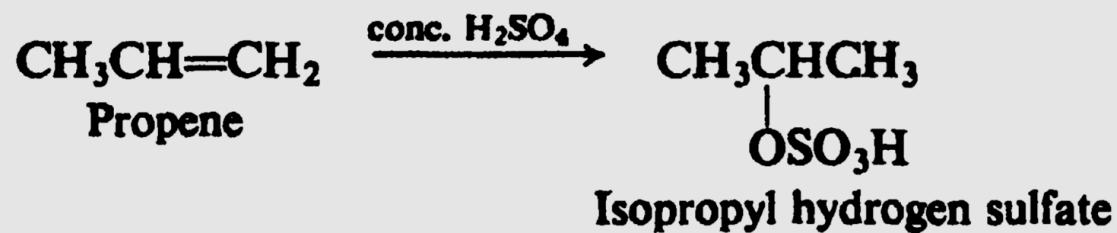
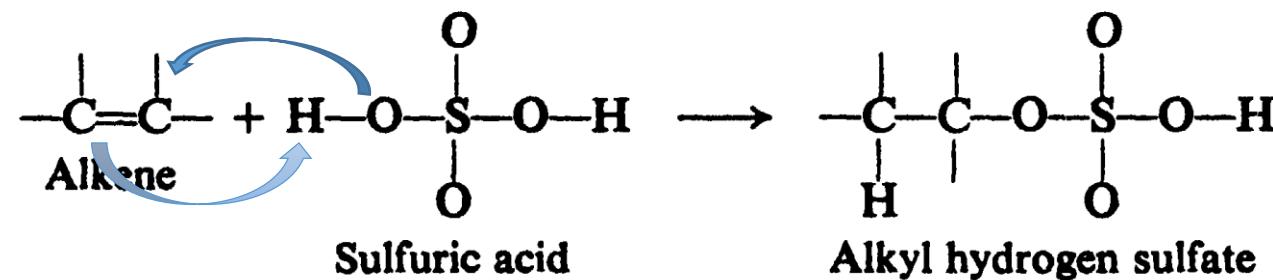


In 2-pentene each of the doubly-bonded carbons holds one hydrogen, so that according to the rule we should expect neither product to predominate. Here again the prediction is essentially correct, roughly equal quantities of the two isomers actually being obtained.

Reactions of the carbon-carbon double bond: ADDITION REACTIONS

5. Addition of sulfuric acid

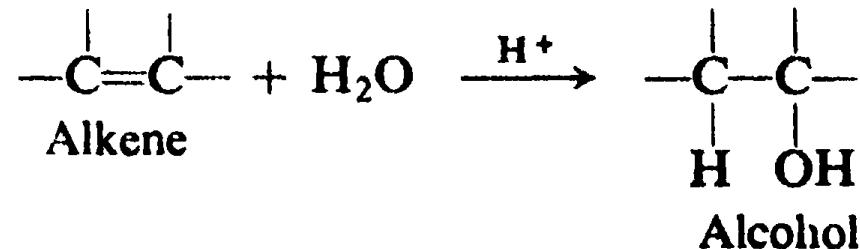
Alkenes react with cold, concentrated sulfuric acid to form compounds of the general formula ROSO_3H , known as **alkyl hydrogen sulfates**. These products are formed by addition of hydrogen ion to one side of the double bond and bisulfate ion to the other following **Markovnikov's rule**. It is important to notice that carbon is bonded to oxygen and not to sulfur.



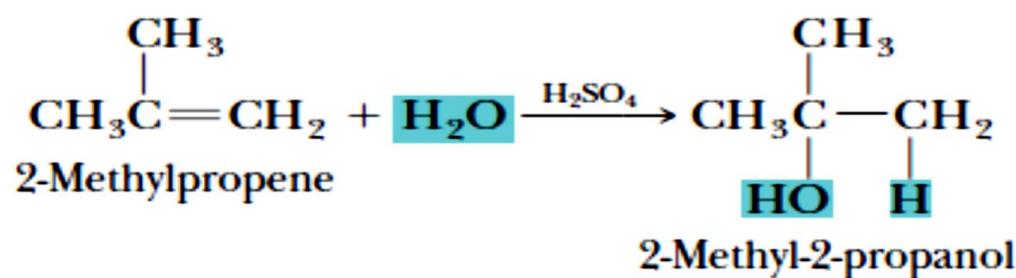
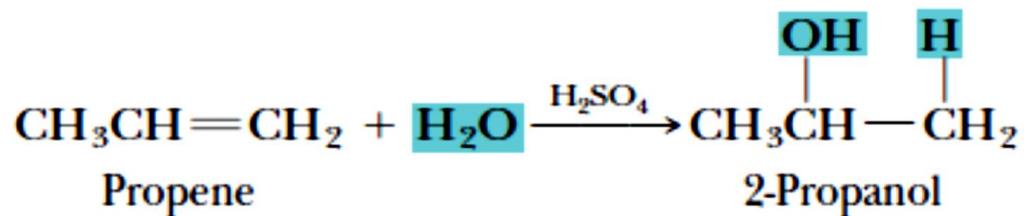
Reactions of the carbon-carbon double bond: ADDITION REACTIONS

6. Addition of water. (Hydration)

Following **Markovnikov's rule**, water adds to the more reactive alkenes in the presence of acids to yield alcohols.



Examples:

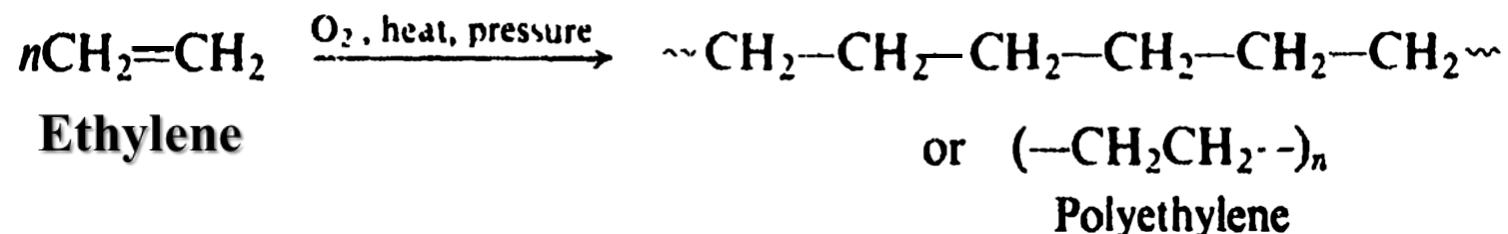


Reactions of the carbon-carbon double bond: ADDITION REACTIONS

7. Polymerization

polymerization is *the joining together of many small molecules to make very large molecules*. The compound composed of these very large molecules is called a **polymer** (Greek: *poly* + *meros*, many parts). The simple compounds from which polymers are made are called **monomers** (*mono* = one).

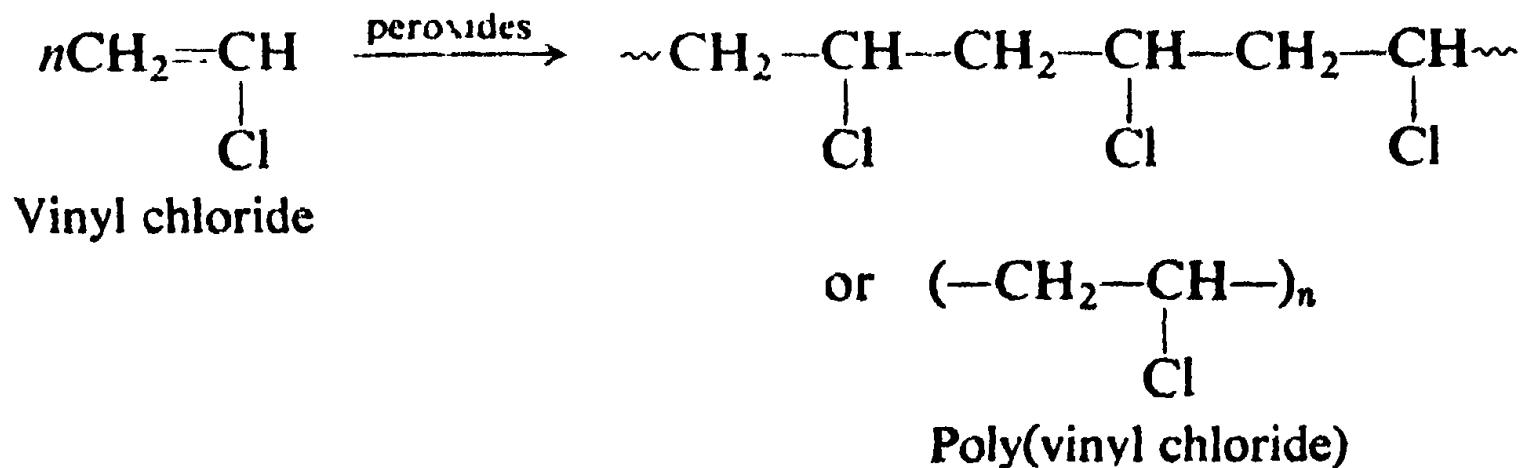
When ethylene is heated under pressure with oxygen, there is obtained a compound of high molecular weight (about 20,000), which is essentially an alkane with a very long chain. This compound is made up of many ethylene units and hence is called polyethylene. It is familiar to most of us as the plastic material of packaging films.



Reactions of the carbon-carbon double bond: ADDITION REACTIONS

Polymerization

Polymerization of substituted ethylenes yields compounds whose structures contain the long chain of polyethylene, with substituents attached at more or less regular intervals. For example, vinyl chloride yields ***poly(vinyl chloride)***, used to make phonograph records, plastic pipe, and when plasticized with high-boiling esters raincoats, shower curtains, and coatings for metals and upholstery fabrics.



Reactions of the carbon-carbon double bond: ADDITION REACTIONS

Polymerization

Recycling Code	Polymer	Common Uses	Uses of Recycled Polymer
1 PET	Poly(ethylene terephthalate)	Soft-drink bottles, household chemical bottles, films, textile fibers	Soft-drink bottles, household chemical bottles, films, textile fibers
2 HDPE	High-density polyethylene	Milk and water jugs, grocery bags, bottles	Bottles, molded containers
3 V	Poly(vinyl chloride), PVC	Shampoo bottles, pipes, shower curtains, vinyl siding, wire insulation, floor tiles, credit cards	Plastic floor mats
4 LDPE	Low-density polyethylene	Shrink wrap, trash and grocery bags, sandwich bags, squeeze bottles	Trash bags and grocery bags
5 PP	Polypropylene	Plastic lids, clothing fibers, bottle caps, toys, diaper linings	Mixed-plastic components
6 PS	Polystyrene	Styrofoam™ cups, egg cartons, disposable utensils, packaging materials, appliances	Molded items such as cafeteria trays, rulers, Frisbees™, trash cans, videocassettes
7	All other plastics and mixed plastics	Various	Plastic lumber, playground equipment, road reflectors

Organic Chemistry for Biology Students

Lecture 5

CHAPTER THREE

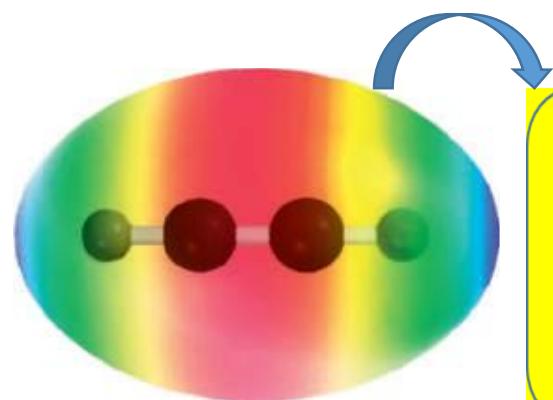
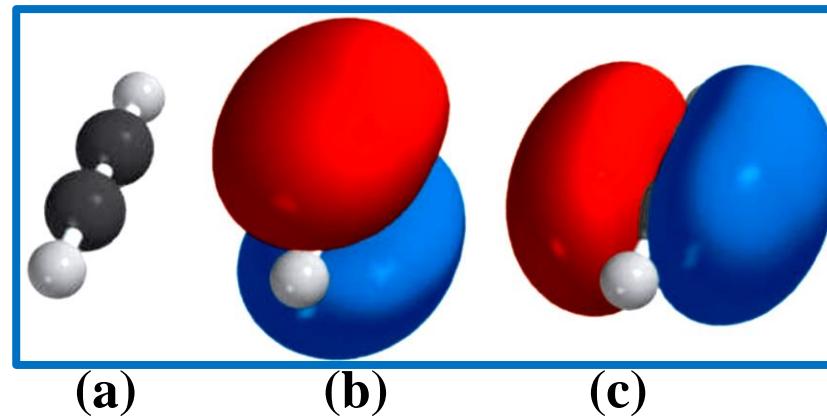
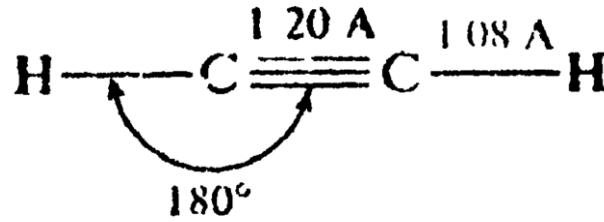
Alkynes

(Structure, Preparation and Reactions)

Dr. Omar Abdulateef

Structure and Bonding in Alkynes

Alkynes are unsaturated hydrocarbons contain at least one **carbon–carbon triple bond**. They have the general formula C_nH_{2n-2} , where $n = 2, 3, \dots$. The simplest alkyne; *Acetylene (ethyne)* C_2H_2 is linear, with a carbon–carbon bond distance of 1.20 Å and carbon–hydrogen bond distances of 1.08 Å, and all of its bond angles are 180° .



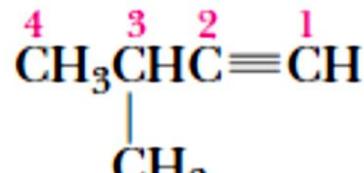
Electrostatic potential map of acetylene.
The region of highest negative charge (red) is associated with the π bonds and lies between the two carbons. Because acetylene has two π bonds, a band of high electron density encircles the molecule.

The carbon atoms of acetylene are connected by a $\sigma + \pi + \pi$ triple bond.
(a) Both carbon atoms are sp-hybridized, and each is bonded to a hydrogen by a σ bond. The two π bonds are **perpendicular** to each other and are shown separately in (b) and (c).

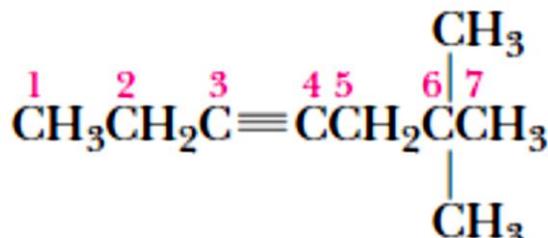
Nomenclature of Alkynes

In naming **alkynes** the usual IUPAC rules are exactly the same as for the naming of alkenes, except that the ending **-yne** replaces **-ene**.

- The parent structure is the longest continuous chain that contains the triple bond.
- We number the longest carbon chain that contains the triple bond from the end that gives the triply bonded carbons the lower set of numbers.
- We indicate the location of the triple bond by the number of the first carbon of the triple bond.



3-Methyl-1-butyne



6,6-Dimethyl-3-heptyne



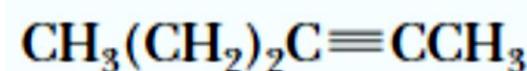
1-Butyne



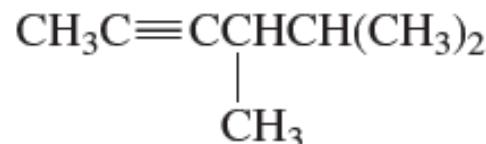
2-Butyne



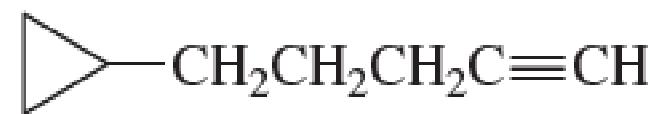
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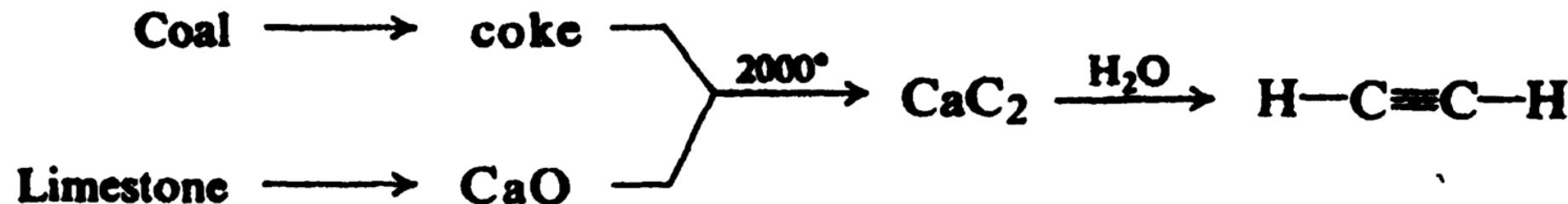


Physical properties of Alkynes

Being compounds of low polarity, the **alkynes** have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ligroin, ether, benzene, carbon tetrachloride. They are less dense than water. **Their boiling points show the usual increase with increasing carbon number**, and the usual effects of chain-branching; they are very nearly the same as the boiling points of alkanes or alkenes with the same carbon skeletons.

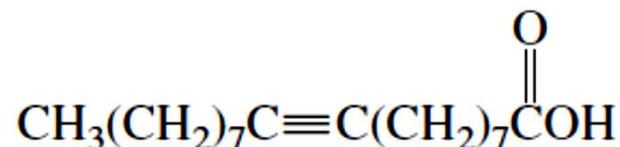
Industrial source of acetylene:

Acetylene is prepared by the reaction between calcium oxide and coke at the very high temperatures of the electric furnace. The calcium oxide and coke are in turn obtained from limestone and coal, respectively. Acetylene is thus obtained by a few steps from three abundant, cheap raw materials: water, coal, limestone.

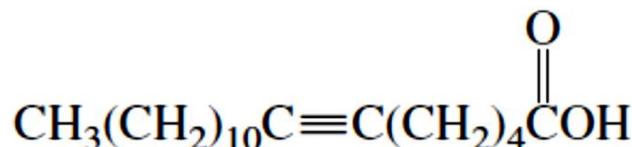


Alkynes in Nature

More than 1000 natural products contain **carbon–carbon triple bonds**. Many, such as stearolic acid and tariric acid, are fatty acids—carboxylic acids with unbranched chains of 12–20 carbon atoms—or are derived from them.

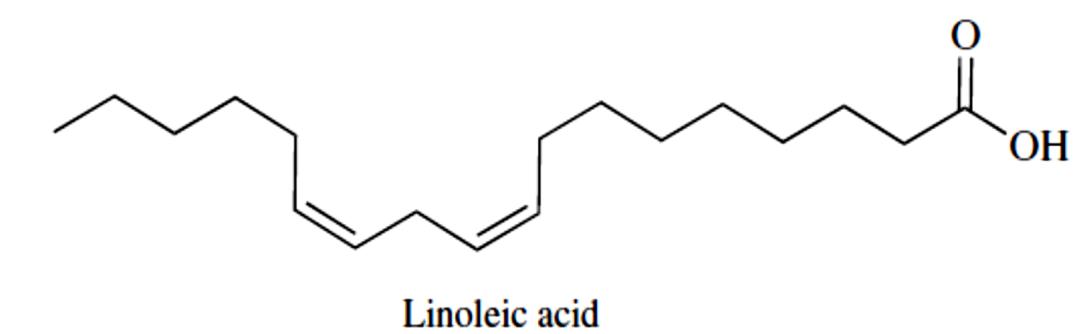
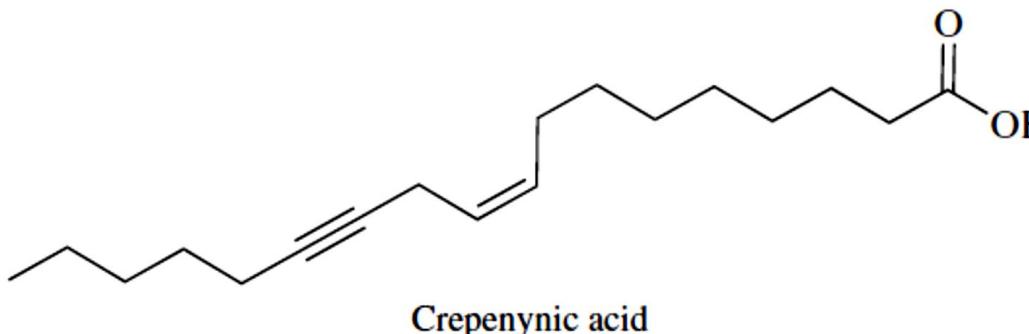


Stearolic acid



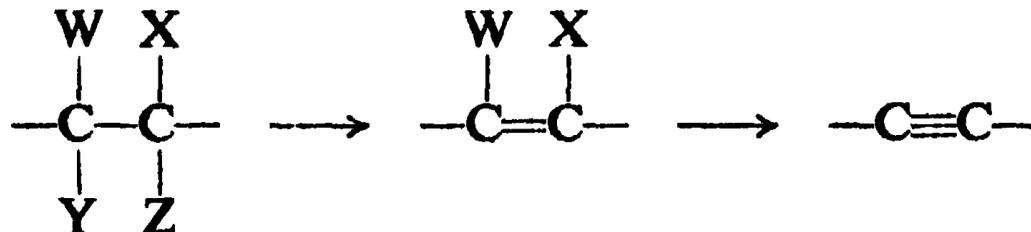
Tariric acid

A major biosynthetic route to **acetylenic fatty acids** in certain **flowering plants** involves oxidation of analogous compounds with carbon–carbon double bonds, and is catalyzed by enzymes of the desaturase class known as acetyleneases. **Crepenynic acid**, which is formed by oxidation of the fatty acid **linoleic acid**, is one example.



Preparation of Alkynes

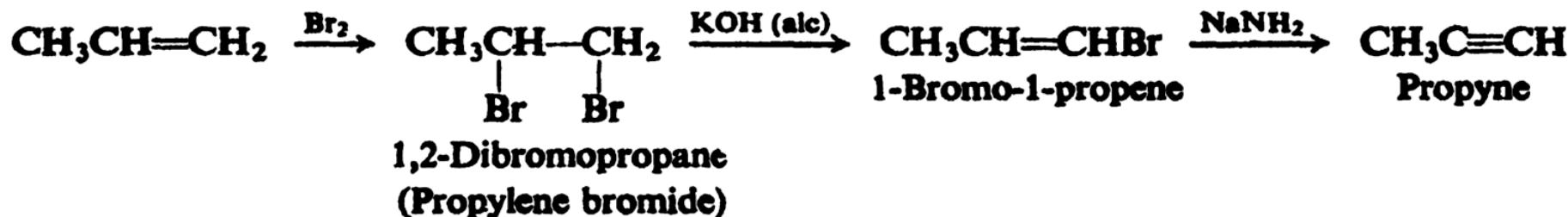
A **carbon-carbon triple bond** is formed in the same way as a double bond: **elimination** of atoms or groups **from two adjacent carbons**. The groups eliminated and the reagents used are essentially the same as in the preparations of alkenes.



1. Dehydrohalogenation of alkyl dihalides: (*Elimination of 2HX*)

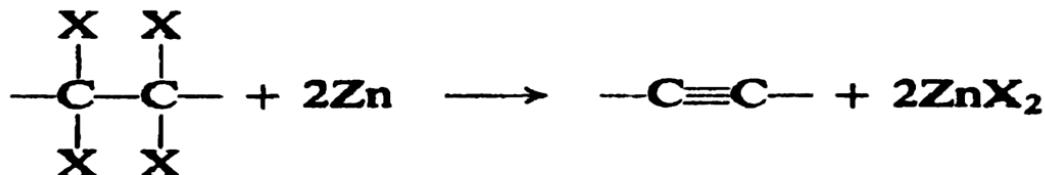


Example:



Preparation of Alkynes

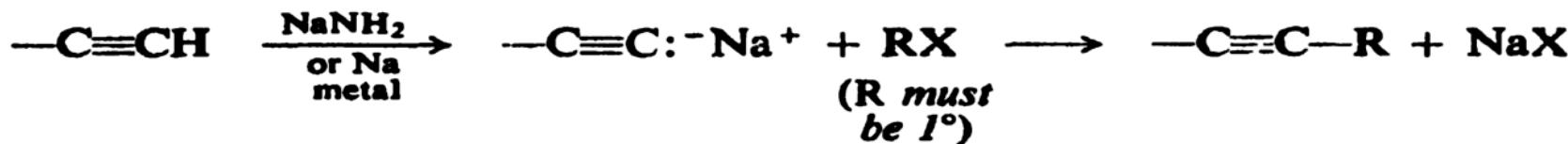
2. Dehalogenation of tetrahalides: (*Elimination of 2 X₂*)



Example:



3. Reaction of sodium acetylides with primary alkyl halides

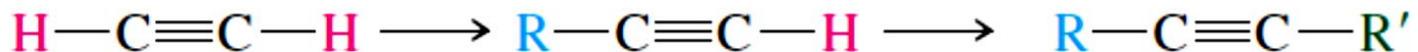


Examples:



Preparation of Alkynes

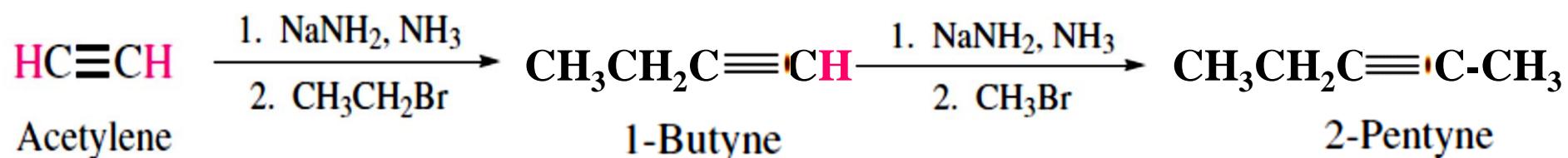
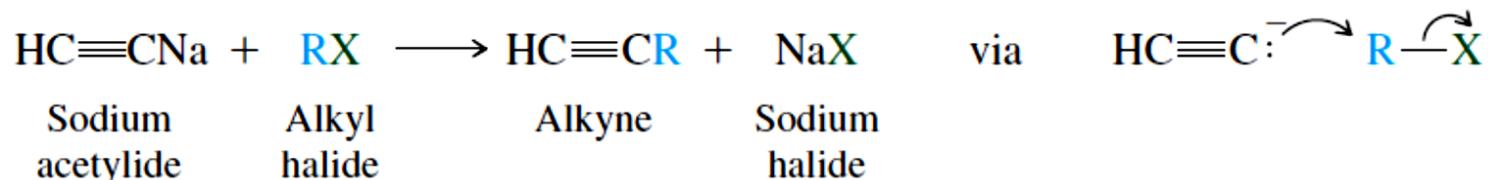
3. Reaction of sodium acetylides with primary alkyl halides: (Examples)



Acetylene

Monosubstituted
or terminal alkyne

Disubstituted
derivative of acetylene



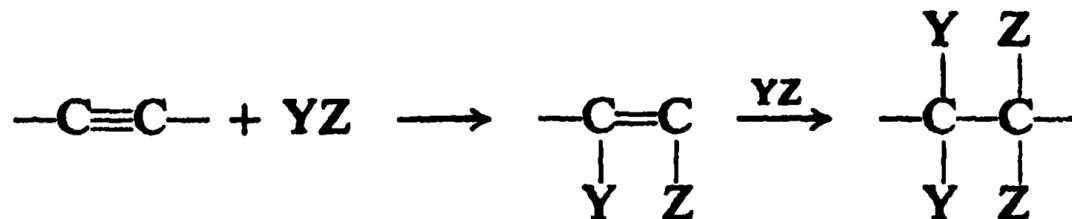
Problem Outline efficient syntheses of each of the following alkynes from acetylene and any necessary organic or inorganic reagents:

- (a) 1-Heptyne
- (b) 2-Heptyne
- (c) 3-Heptyne

Reactions of Alkynes

Alkynes undergo two types of reactions: *Addition Reactions* and *Reactions as Acids*

Addition Reactions: Just like alkenes, alkynes undergo **electrophilic addition**, and for the same reason: availability of the loosely held π electrons.



Addition of **hydrogen**, **halogens**, and **hydrogen halides** to alkynes is very much like addition to alkenes, except that here **two molecules** of reagent can be consumed for each triple bond.

Reactions as Acids: Alkynes undergo certain reactions that are due to the **acidity** of a **hydrogen** atom held by triply-bonded carbon.

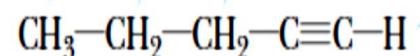


Acetylene



Monosubstituted
or terminal alkyne

these hydrogens are much lower in acidity and are not deprotonated by NaNH_2

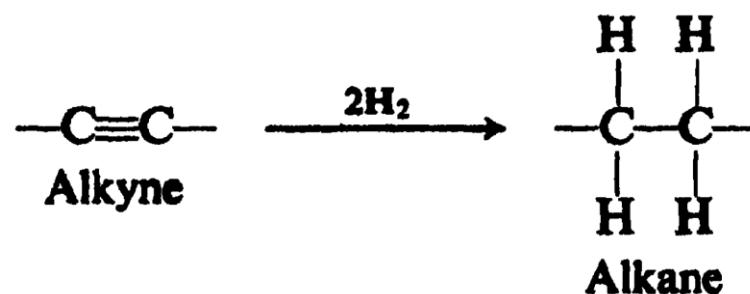


only this hydrogen is acidic enough to be deprotonated by NaNH_2

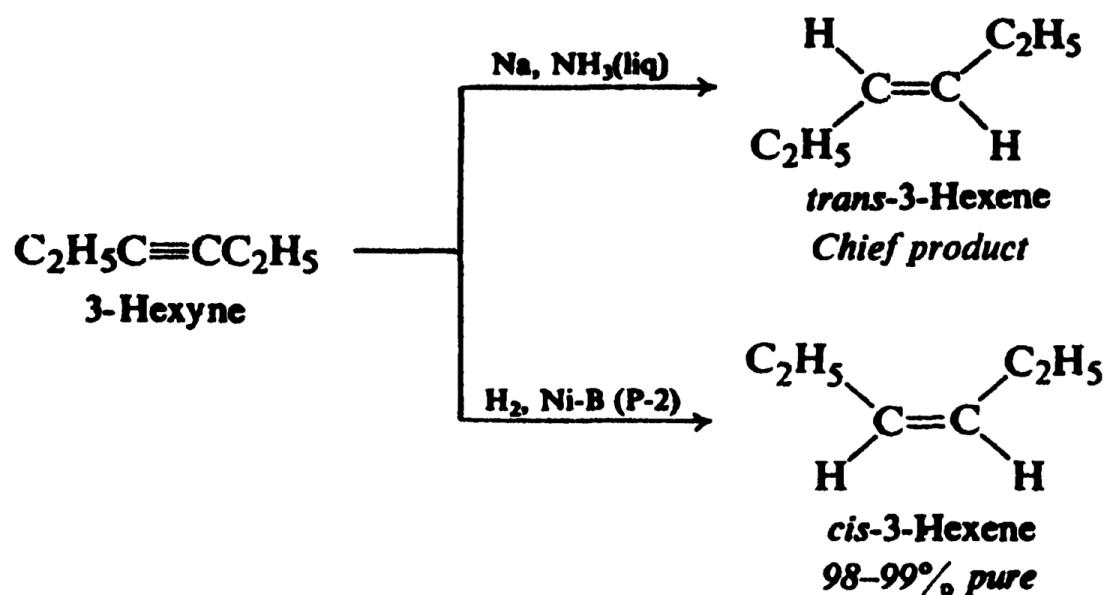
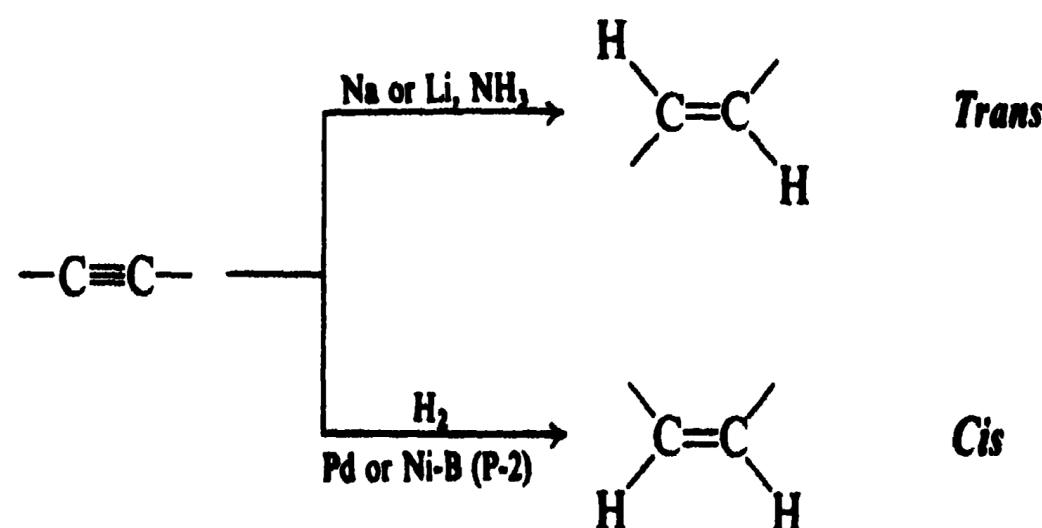
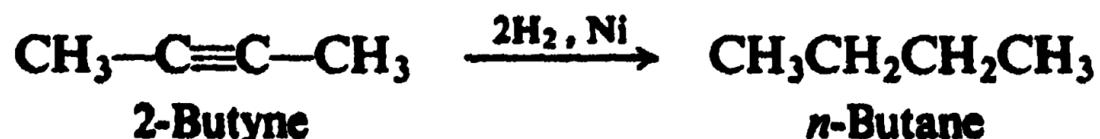
Reactions of Alkynes

Addition Reactions

1. Addition of hydrogen:

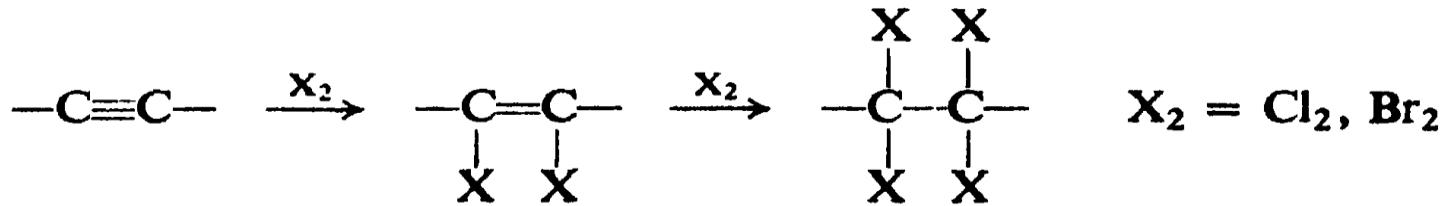


Example:

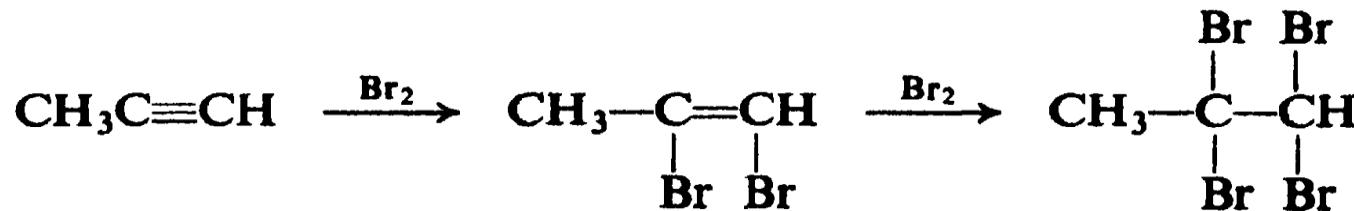


Reactions of Alkynes

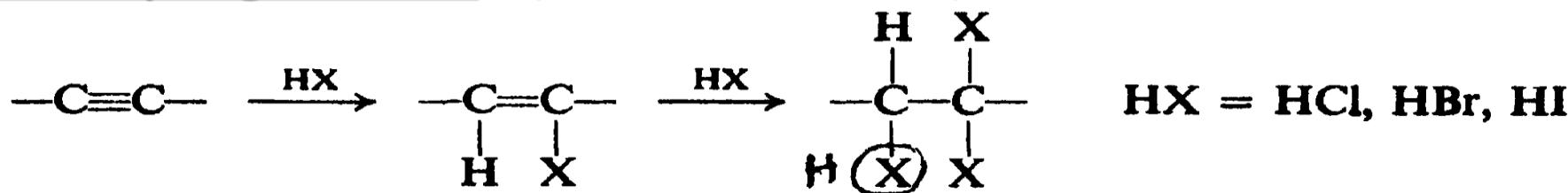
2. Addition of halogens



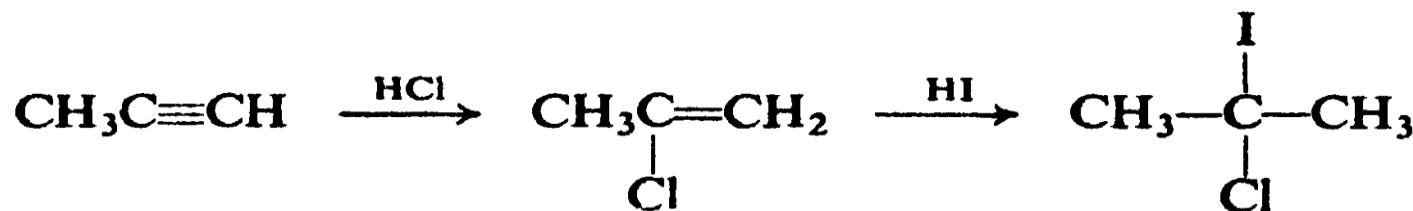
Example:



3. Addition of hydrogen halides: (Markovnikov's Rule)



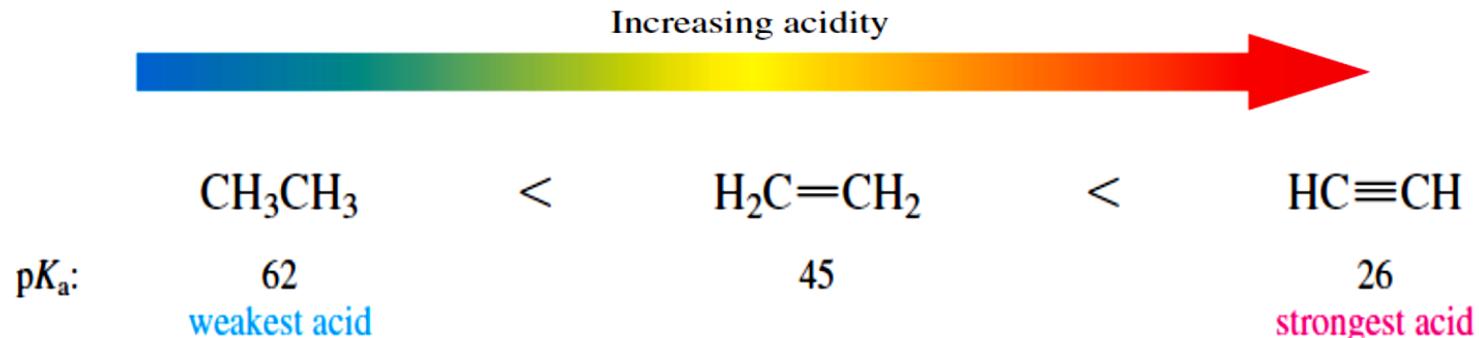
Example:



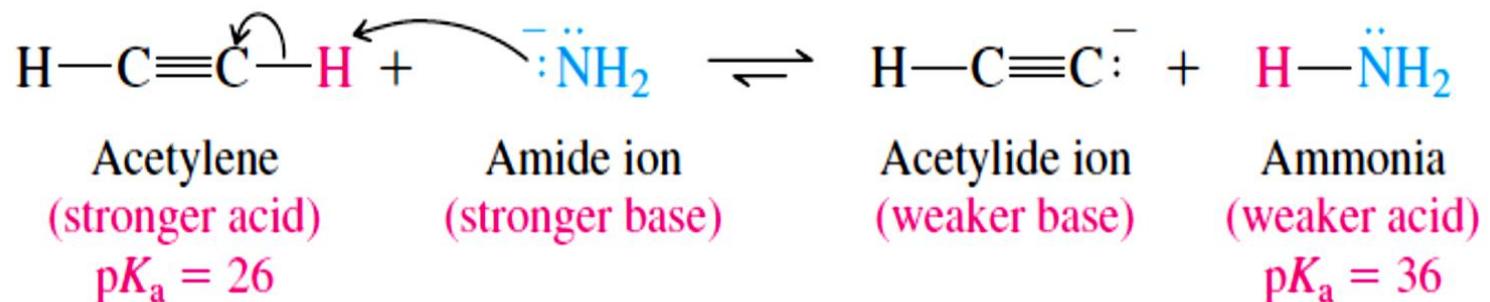
Reactions of Alkynes

Reactions as Acids

According to the **Lowry-Bronsted definition** of acids; **acidity is a measure of the tendency of a compound to lose a hydrogen ion.** The C–H bonds of hydrocarbons show little tendency to ionize, and alkanes, alkenes, and alkynes are all very weak acids. However, **acetylene** and **terminal alkynes are far stronger acids than other hydrocarbons.**



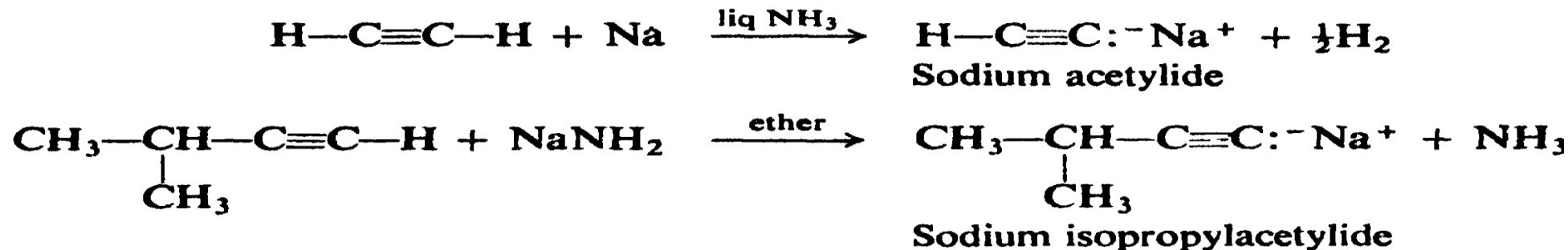
Thus, **acetylene** and **terminal alkynes** react with a strong base (such as alkali metals or NaNH_2) to form alkali metal acetylides (page 9).



Reactions of Alkynes

Formation of alkali metal acetylides

Examples:



Problems:

1. Show by writing appropriate chemical equations how each of the following compounds could be converted to 1-hexyne:
 - (a) 1,1-Dichlorohexane
 - (b) 1-Hexene
 - (c) Acetylene
 - (d) 1-Iodohexane

2. Show by writing appropriate chemical equations how each of the following compounds could be converted to 3-hexyne:
 - (a) 1-Butene
 - (b) 1,1-Dichlorobutane
 - (c) Acetylene

Organic Chemistry for Biology Students

Lecture 6

CHAPTER FOUR

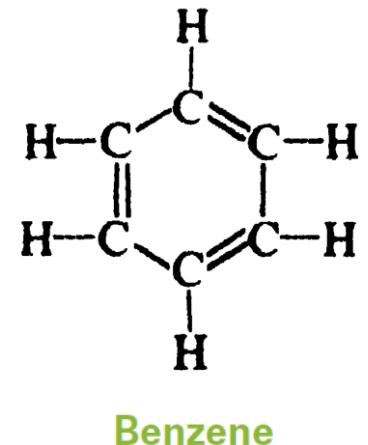
Aromatic Hydrocarbons

Benzene and Its Derivatives

Dr. Omar Abdulateef

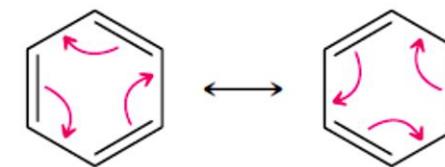
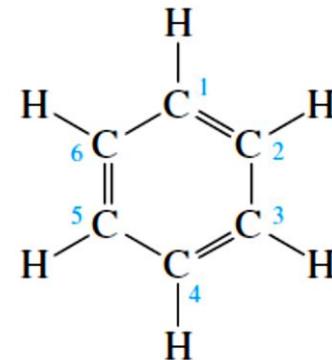
Aromatic Compounds

- **Aromatic compounds** are organic compounds containing **benzene ring** and/or compounds that resemble **benzene** in chemical behavior.
- **Benzene** was isolated from **coal tar** by August W. von Hofmann in 1845. Coal tar remained the primary source for the industrial production of benzene for many years, until petroleum-based technologies became competitive about 1950.
- Aromatic properties are those properties of **benzene** that distinguish it from **aliphatic hydrocarbons**.
- The original meanings (**old meaning**) of the words "**aliphatic**" (**fatty; oily**) and "**aromatic**" (**fragrant; odorous**) no longer have any significance.
- **Aliphatic hydrocarbons** (alkanes, alkenes, alkynes, and their cyclic forms), as we have seen, undergo chiefly **addition** and **free-radical substitution**; addition occurs at multiple bonds (**alkenes & alkynes**), and free-radical substitution occurs at other points along the aliphatic chain (**alkanes**).
- In contrast, we shall find that **aromatic hydrocarbons** are characterized by a tendency to undergo **ionic substitution**.

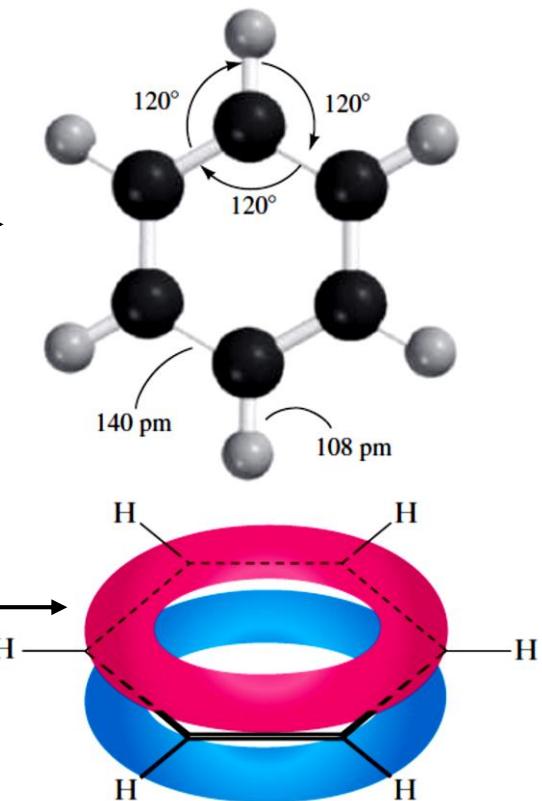


Structure of Benzene

- **Benzene** has the molecular formula C_6H_6 .
- The six carbon atoms of benzene were joined together in a ring. Four bonds to each carbon could be accommodated by a system of alternating single and double bonds with one hydrogen on each carbon.
- Benzene is planar and has the shape of a regular hexagon.
- All of the carbon–carbon bonds are the same length (140 pm) and the 120° bond angles. Also, all of C–H bonds are the same length (108 pm).
- The electron density of the π system lies in one torus above the plane of the ring and a second torus below the plane.
- π electrons are *delocalized* over a cyclic conjugated system.
- Electron delocalization leads to **increase stability** of benzene.
- Stabilization energy of benzene is called **RESONANCE ENERGY** which is responsible for the new set of properties we call **aromatic properties**.



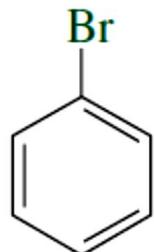
Benzene as a hybrid of two equivalent contributing structures



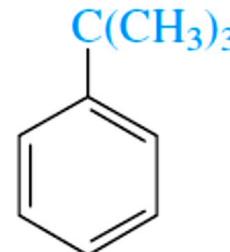
Nomenclature of Benzene Derivatives

A. Monosubstituted Benzenes:

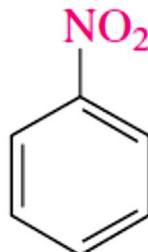
- For many of these derivatives we simply *prefix* the name of the substituent group to the word **benzene**, as for example in **chlorobenzene**, **bromobenzene**, **iodobenzene**, **nitrobenzene**, **ethylbenzene** and so on.



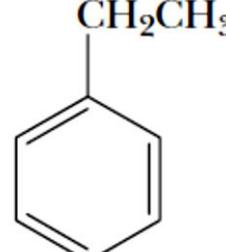
Bromobenzene



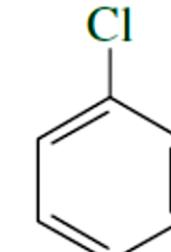
tert-Butylbenzene



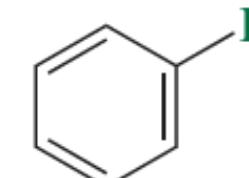
Nitrobenzene



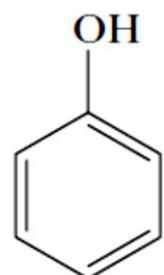
Ethylbenzene



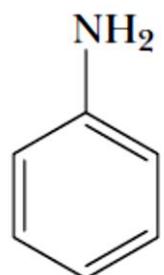
Chlorobenzene



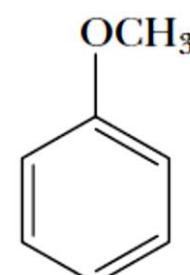
Iodobenzene



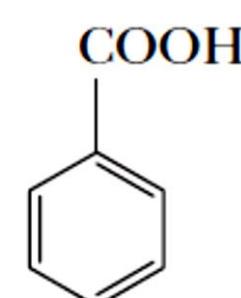
Phenol



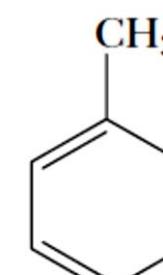
Aniline



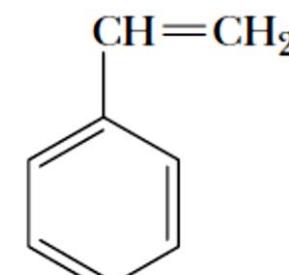
Anisole



Benzoic acid



Toluene

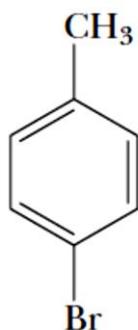


Styrene

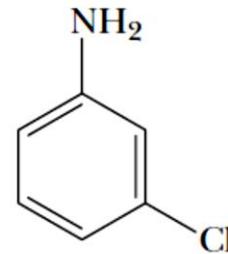
Nomenclature of Benzene Derivatives

B. Disubstituted Benzenes:

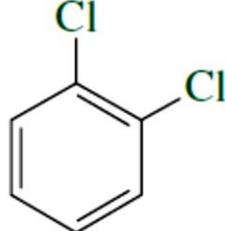
- We locate substituents either by **numbering** the atoms of the ring or by using the locators ***ortho***, ***meta***, and ***para***.
- When one of the two substituents on the ring imparts a **special name** to the compound, as, for example, **toluene**, **phenol**, and **aniline** (page4), then we name the compound as a derivative of that parent molecule. In this case, the special substituent occupies ring position number **1**.



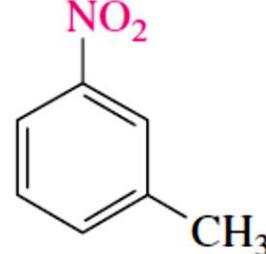
4-Bromotoluene
(*p*-Bromotoluene)



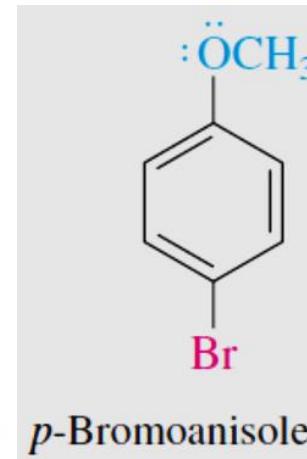
3-Chloroaniline
(*m*-Chloroaniline)



o-Dichlorobenzene
(1,2-dichlorobenzene)



m-Nitrotoluene
(3-nitrotoluene)



p-Bromoanisole

Ortho (o) Refers to groups occupying positions **1** and **2** on a benzene ring.

Meta (m) Refers to groups occupying positions **1** and **3** on a benzene ring.

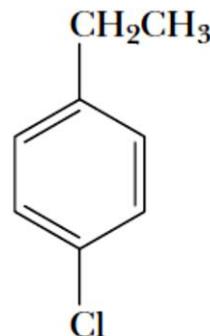
Para (p) Refers to groups occupying positions **1** and **4** on a benzene ring.

- The ***o***, ***m***, and ***p*** prefixes are not used when three or more substituents are present on benzene; numerical locants must be used instead.

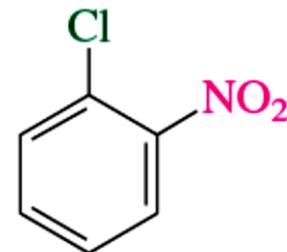
Nomenclature of Benzene Derivatives

B. Disubstituted Benzenes:

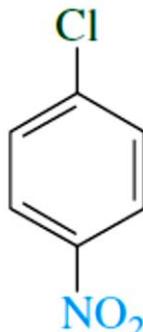
- When none of special substituents are present, we locate the two substituents (using **numbers** or ***o*-, *m*-, *p*-locators**) and list them in alphabetical order before the ending -benzene. The carbon of the benzene ring with the substituent of lower alphabetical ranking is numbered C-1.



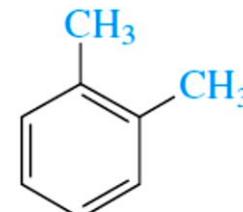
1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)



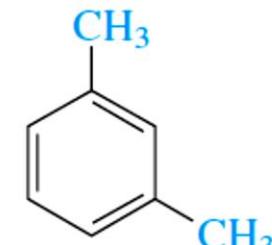
o-Chloronitrobenzene
(1-Chloro-2-nitrobenzene)



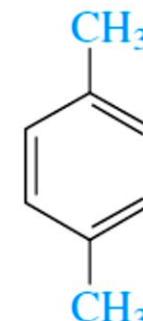
1-Chloro-
4-nitrobenzene



o-Xylene
(1,2-dimethylbenzene)



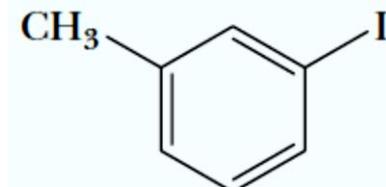
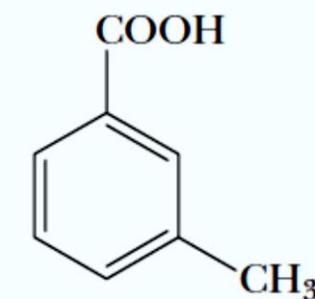
m-Xylene
(1,3-dimethylbenzene)



p-Xylene
(1,4-dimethylbenzene)

Problem: Write a structural formula for each of the following compounds:

- (a) ***o*-Ethylanisole** (b) **3-Chlorostyrene**
(b) (c) ***p*-Nitroaniline** (d) **4-Chlorophenol**
(e) ***p*-Diisopropylbenzene** (f) **2-Ethylbenzoic acid**

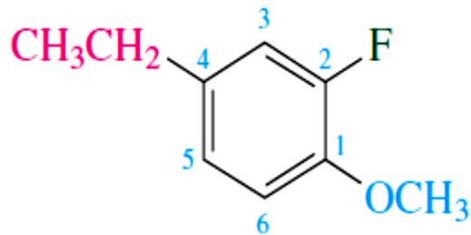


Nomenclature of Benzene Derivatives

C. Polysubstituted Benzenes:

- When three or more substituents are present on a ring, we specify their locations by numbers.
- If one of the substituents imparts a special name, then the molecule is named as a derivative of that parent molecule. In this case, the special substituent occupies ring position number 1. The direction of numbering is chosen to give the next substituted position the lowest number.

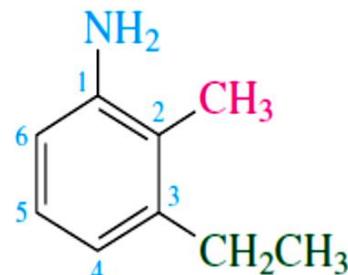
The order of appearance of substituents in the name is alphabetical.



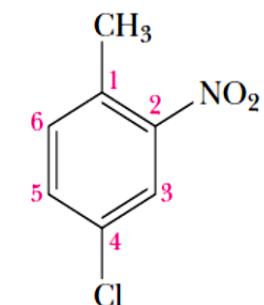
4-Ethyl-2-fluoroanisole



2,4,6-Trinitrotoluene



3-Ethyl-2-methylaniline



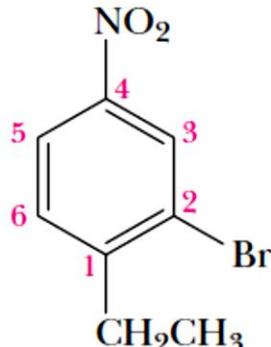
4-Chloro-2-nitrotoluene

The *o*, *m*, and *p* prefixes are not used when three or more substituents are present on benzene; numerical locants must be used instead.

Nomenclature of Benzene Derivatives

C. Polysubstituted Benzenes:

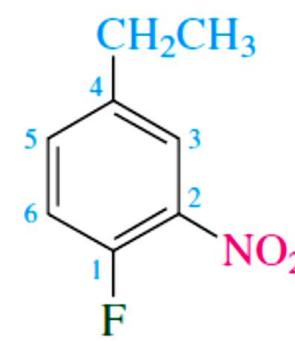
2) If none of the substituents imparts a special name, we number them to give the smallest set of numbers and list them in alphabetical order before the ending -benzene.



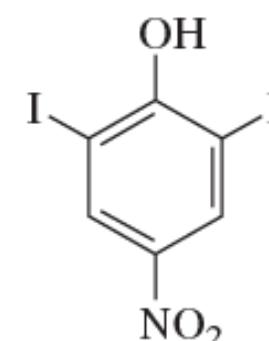
2-Bromo-1-ethyl-4-nitrobenzene



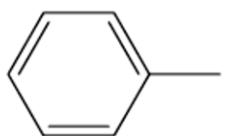
1-Chloro-2,4-dinitrobenzene



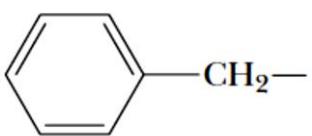
4-Ethyl-1-fluoro-2-nitrobenzene



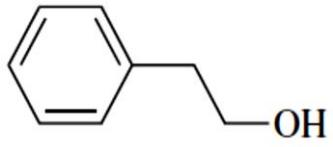
- When the benzene ring is named as a substituent, the word **phenyl** stands for C_6H_5 , a **benzyl** group is $\text{C}_6\text{H}_5\text{CH}_2$.



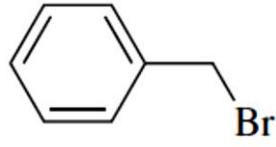
Phenyl group (Ph)



Benzyl group (Bn)



2-Phenylethanol



Benzyl bromide

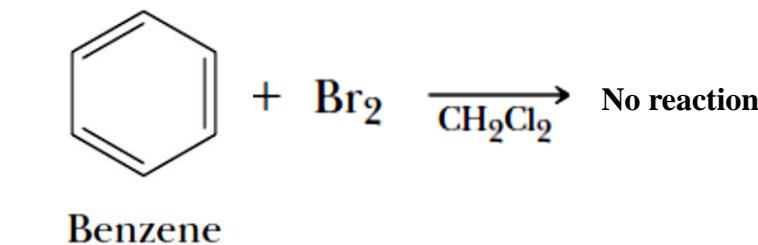
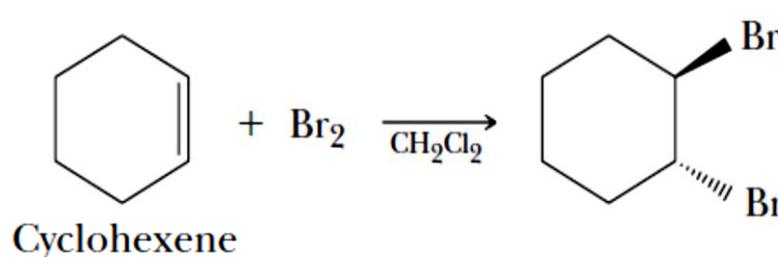
Homework

Write a structural formula for each of the following:

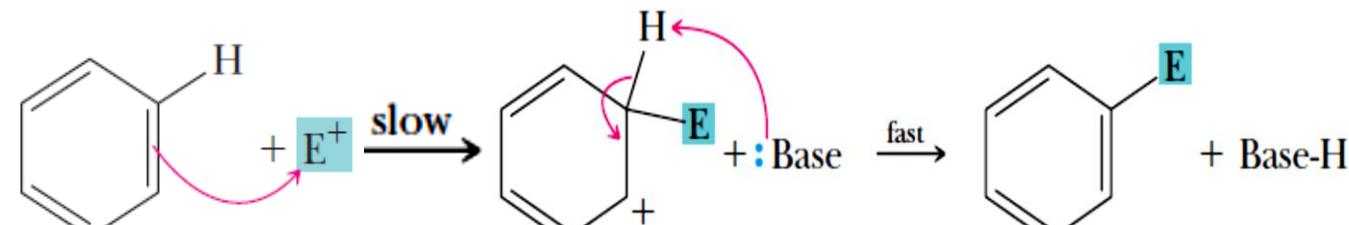
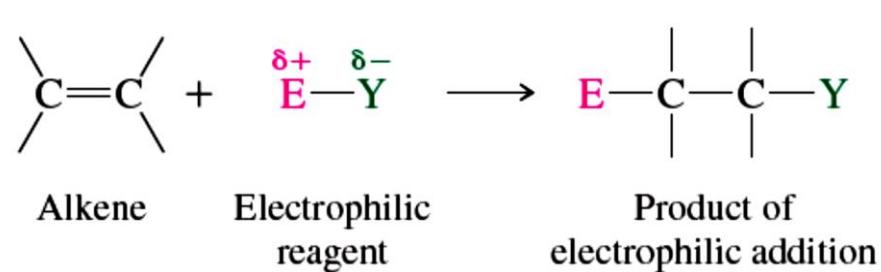
- (a) 1-Phenyl-1-butene (b) 2,4,6-Tribromoaniline
(c) 2-Phenyl-2-butene (d) 4-Bromo-3-ethylstyrene
(e) 1-Phenylethanol
(f) 2-amino-5-bromo-3-nitrobenzoic acid

Reactions of Benzene; Electrophilic Aromatic Substitution

- Benzene undergoes **substitution reactions** instead of **addition reactions**.
- Electron delocalization of π system in benzene ring** leads to unusual stability of the benzene towards electrophilic reagents in contrast to alkenes.



Reagent	Cyclohexene gives	Benzene gives
KMnO_4 (cold, dilute, aqueous)	Rapid oxidation	No reaction
Br_2/CCl_4 (in the dark)	Rapid addition	No reaction
HI	Rapid addition	No reaction
$\text{H}_2 + \text{Ni}$	Rapid hydrogenation	Slow hydrogenation

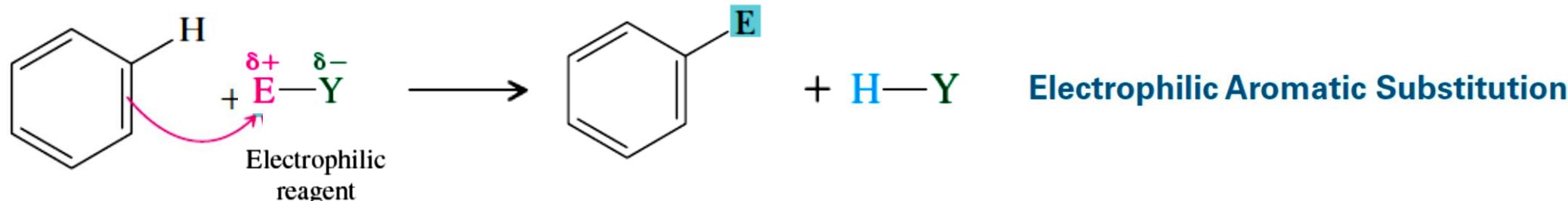


Electrophilic Addition

Electrophilic Aromatic Substitution

Reactions of Benzene; Electrophilic Aromatic Substitution

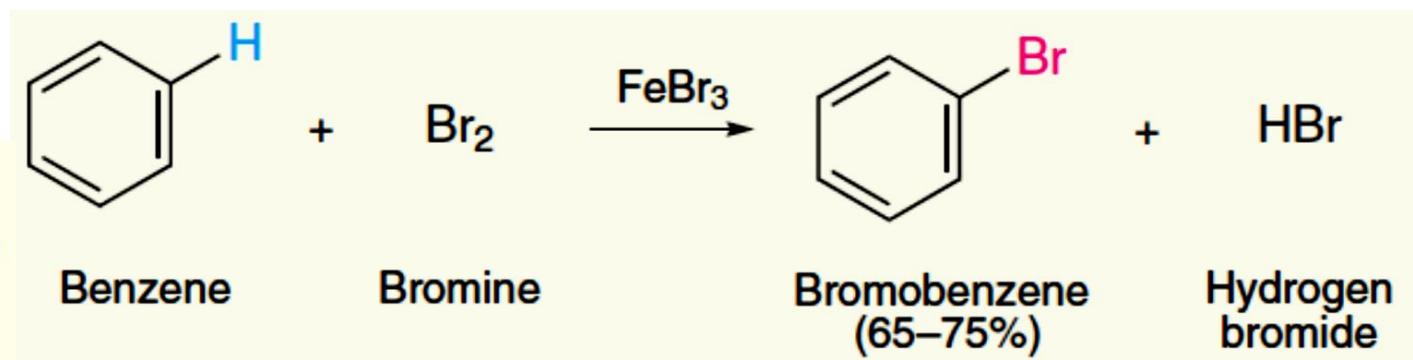
Electrophilic Aromatic Substitution: The electrophilic portion of the reagent (E) replaces one of the hydrogens on the ring.



Some groups that can be introduced directly onto the ring are the halogens (Cl, Br, I), the nitro ($-NO_2$) group, the sulfonic acid ($-SO_3H$) group, alkyl ($-R$) groups, and acyl ($RCO-$) groups.

1. Halogenation:

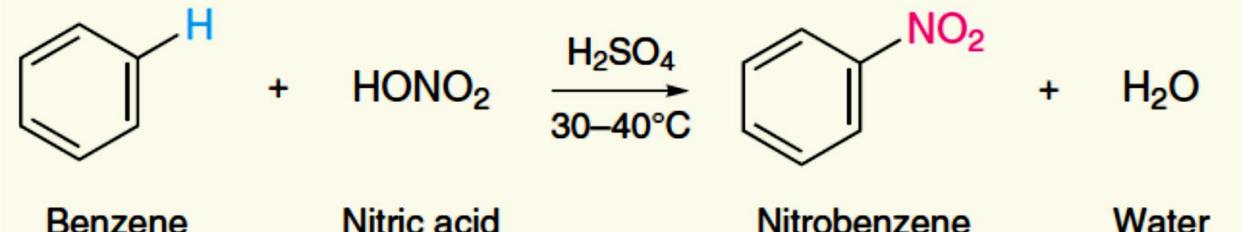
Halogenation Bromine reacts with benzene in the presence of iron(III) bromide as a catalyst to give bromobenzene. Chlorine reacts similarly in the presence of iron(III) chloride to give chlorobenzene.



Reactions of Benzene; Electrophilic Aromatic Substitution

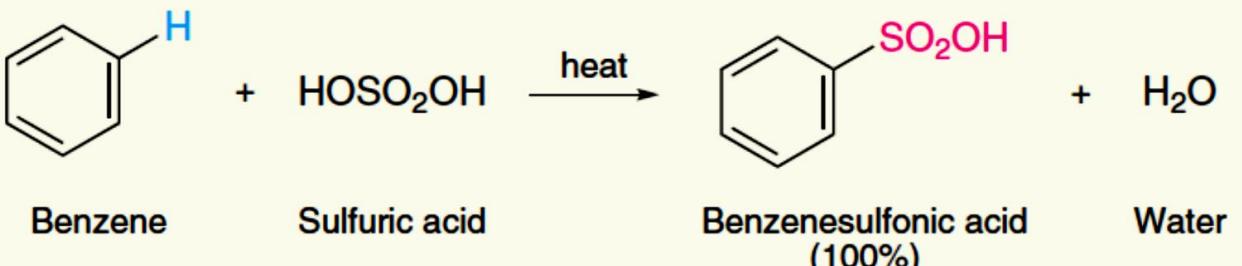
2. Nitration:

Nitration Warming benzene with a mixture of nitric acid and sulfuric acid gives nitrobenzene. A nitro group ($-\text{NO}_2$) replaces one of the ring hydrogens.



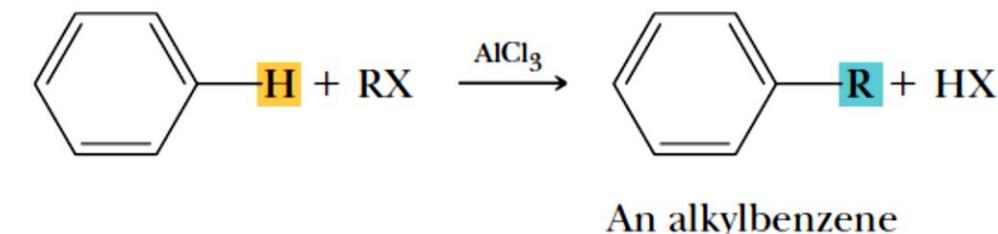
3. Sulfonation:

Sulfonation Treatment of benzene with hot concentrated sulfuric acid gives benzenesulfonic acid. A sulfonic acid group ($-\text{SO}_3\text{OH}$) replaces one of the ring hydrogens.



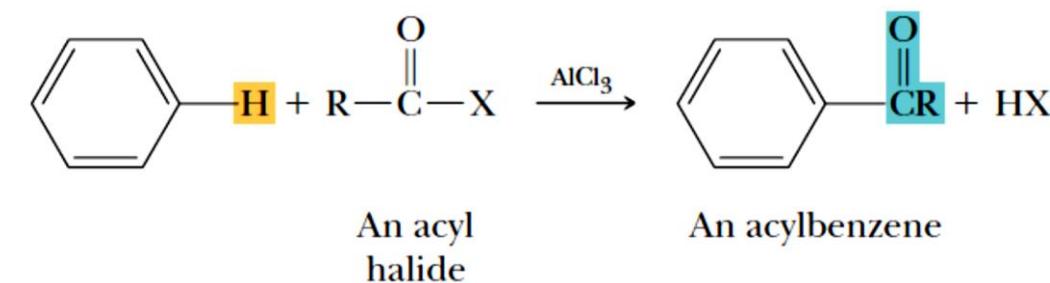
4. Alkylation:

Friedel–Crafts alkylation Alkyl halides react with benzene in the presence of aluminum chloride to yield alkylbenzenes.



5. Acylation:

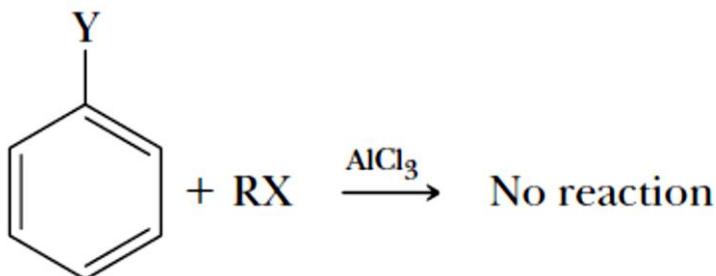
Friedel–Crafts acylation An analogous reaction occurs when acyl halides react with benzene in the presence of aluminum chloride. The products are aryl ketones.



Reactions of Benzene; *Electrophilic Aromatic Substitution*

Limitations on Friedel–Crafts alkylations:

1. The alkyl halide (**RX**) used in the reaction is preferably **3° or 2°**.
2. Benzene ring bearing one or more of the following groups does not undergo Friedel–Crafts alkylation.



When Y Equals Any of These Groups, the Benzene Ring Does Not Undergo Friedel–Crafts Alkylation

$-\text{CH}_2\text{O}-$	$-\text{CR}_2\text{O}-$	$-\text{COOH}$	$-\text{COR}$	$-\text{CONH}_2$
$-\text{SO}_3\text{H}$	$-\text{C}\equiv\text{N}$	$-\text{NO}_2$	$-\text{NR}_3^+$	
$-\text{CF}_3$	$-\text{CCl}_3$			

Organic Chemistry for Biology Students

Lecture 7

CHAPTER FIVE

Aromatic Hydrocarbons

Benzene Derivatives; Reactivity and Orientation

Dr. Omar Abdulateef

Electrophilic Aromatic Substitution of Benzene Derivatives

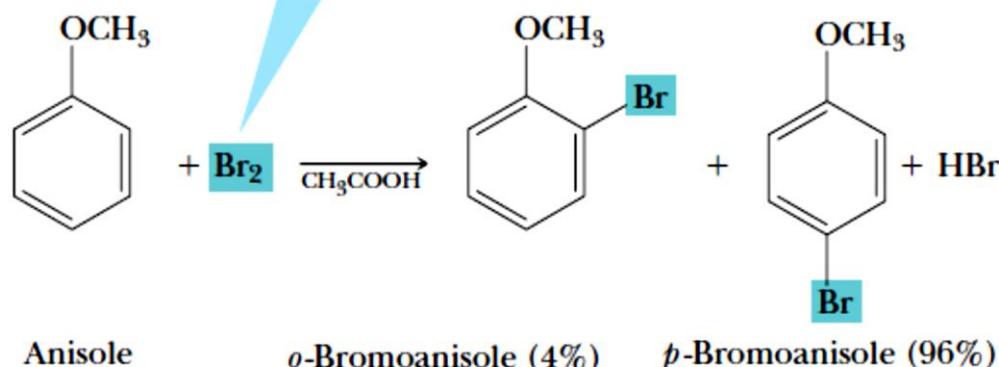
Effect of substituent groups

So far we've been concerned only with electrophilic substitution of benzene. **What about substituted benzene?** Two important questions arise when we turn to substitution on rings that already bear at least one substituent:

1. **What is the effect of a substituent on the *RATE* of electrophilic aromatic substitution?**
2. **What is the effect of a substituent on the *ORIENTATION* of further substitution?**

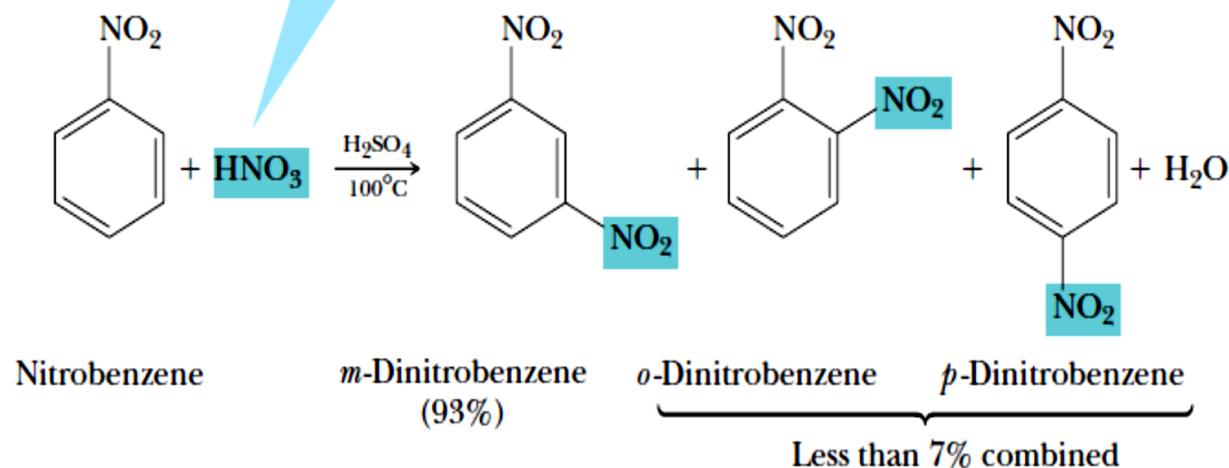
Bromination of anisole proceeds at a rate 1.8×10^9 greater than that of bromination of benzene (the methoxy group is activating), the product is a mixture of *o*-bromoanisole and *p*-bromoanisole (the methoxy group is ortho–para directing)

the bromination of anisole proceeds many times faster than the bromination of benzene. In fact, $-\text{OCH}_3$ is so activating that no catalyst is necessary in this reaction



Nitration of nitrobenzene proceeds 10,000 times slower than the nitration of benzene itself. (A nitro group is strongly deactivating). The product consists of approximately 93% of the meta isomer and less than 7% of the ortho and para isomers combined (the nitro group is meta directing).

the nitration of nitrobenzene proceeds many times slower than the nitration of benzene



Electrophilic Aromatic Substitution of Benzene Derivatives

Classification of substituent groups

- A group is classified as **ACTIVATING** if the ring it is attached to is *more reactive than benzene*.
- A group is classified as **DEACTIVATING** if the ring it is attached to is *less reactive than benzene*.

Activating group

Any substituent on a benzene ring that causes the rate of electrophilic aromatic substitution to be greater than that for benzene.

Deactivating group

Any substituent on a benzene ring that causes the rate of electrophilic aromatic substitution to be lower than that for benzene.

1. All activating substituents are *ortho-para* directing.
2. Halogen substituents are slightly deactivating but are *ortho-para* directing.
3. Strongly deactivating substituents are *meta* directors.

Electrophilic Aromatic Substitution of Benzene Derivatives

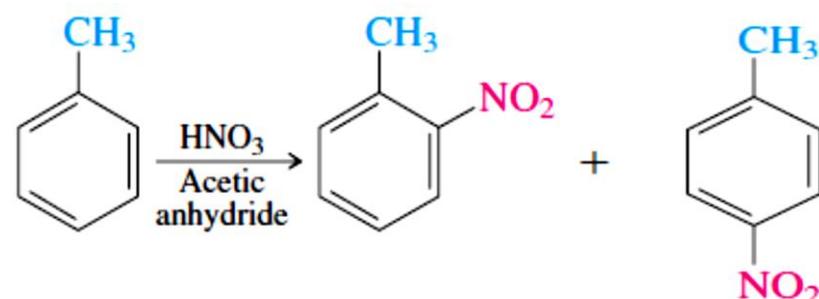
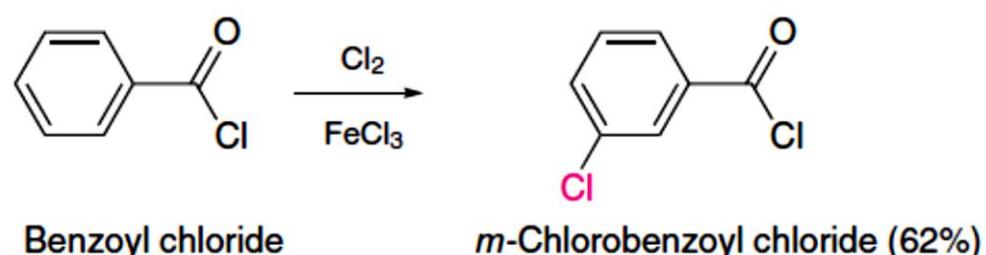
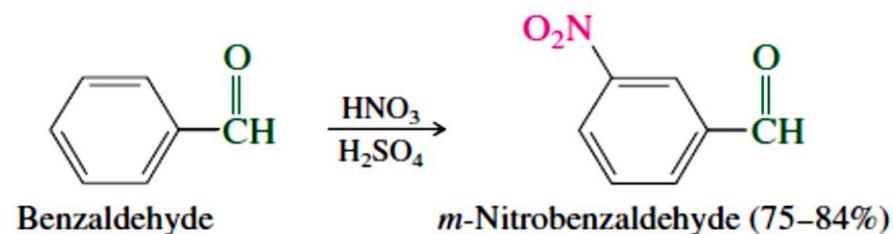
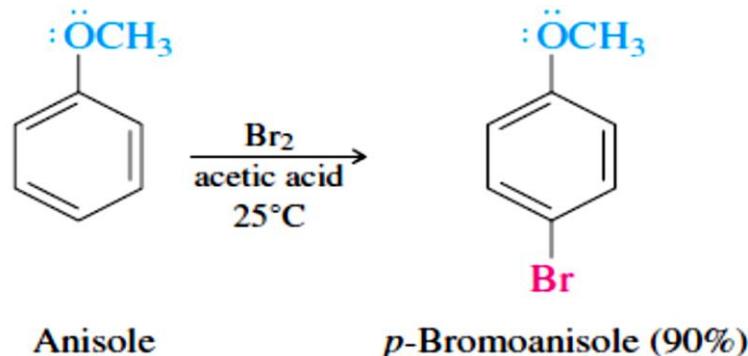
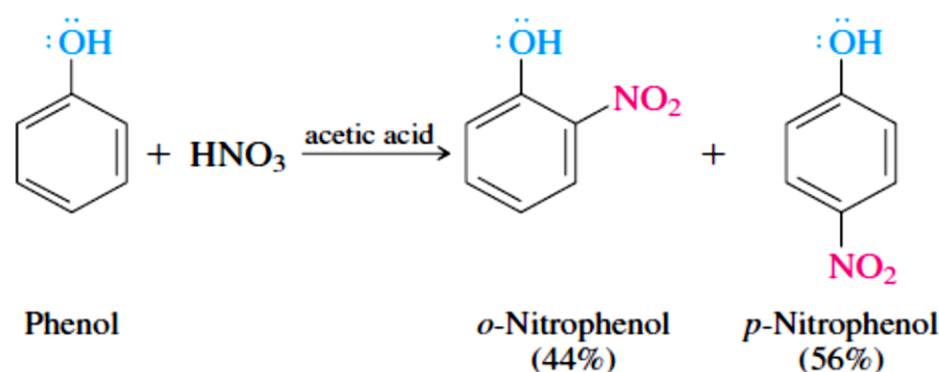
Classification of substituent groups

(مهم جداً يحفظ) Table (5. 1) Effects of Substituents on Further Electrophilic Aromatic Substitution

Ortho-Para Directing	strongly activating	$-\ddot{\text{N}}\text{H}_2$	$-\ddot{\text{N}}\text{HR}$	$-\ddot{\text{N}}\text{R}_2$	$-\ddot{\text{O}}\text{H}$	$-\ddot{\text{O}}\text{R}$	
	moderately activating	$-\ddot{\text{N}}\text{HC}\equiv\text{R}$	$-\ddot{\text{N}}\text{HC}\equiv\text{Ar}$	$-\ddot{\text{O}}\text{C}\equiv\text{R}$	$-\ddot{\text{O}}\text{C}\equiv\text{Ar}$		
	weakly activating	$-\text{R}$					
	weakly deactivating	$-\text{F}$	$-\text{Cl}$	$-\text{Br}$	$-\text{I}$		
Meta Directing	moderately deactivating	$-\text{CH}$	$-\text{CR}$	$-\text{COH}$	$-\text{COR}$	$-\text{CNH}_2$	$-\text{SOH}$
	strongly deactivating	$-\text{NO}_2$	$-\text{NH}_3^+$	$-\text{CF}_3$	$-\text{CCl}_3$		

Electrophilic Aromatic Substitution of Benzene Derivatives

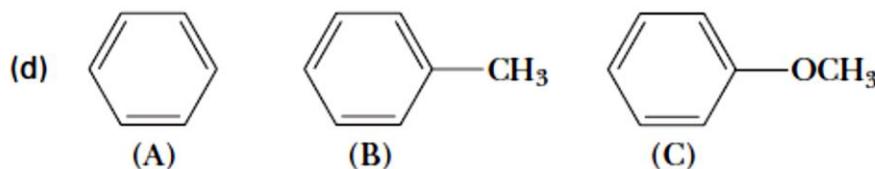
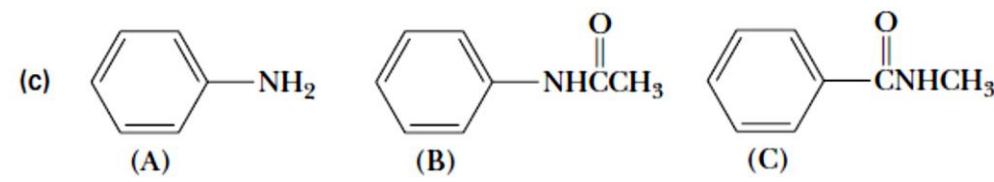
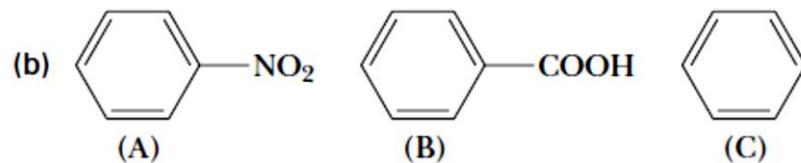
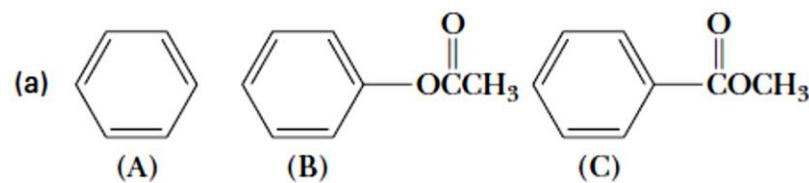
Examples:



Electrophilic Aromatic Substitution of Benzene Derivatives

Problem (5.1):

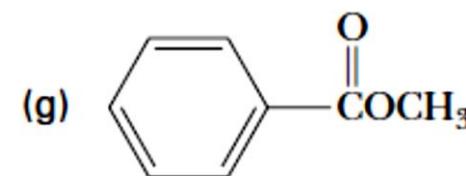
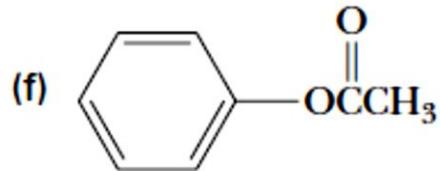
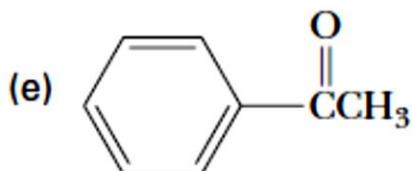
(1) Arrange the compounds in each set in order of decreasing reactivity (fastest to slowest) toward electrophilic aromatic substitution:



(2) Draw the structural formula for the major product formed upon treating each compound with $\text{Cl}_2/\text{FeCl}_3$:

- (a) Toluene
(c) Chlorobenzene

- (b) Nitrobenzene
(d) *tert*-Butylbenzene



(h) Benzenesulfonic acid

Benzene Derivatives; Orientation and Synthesis

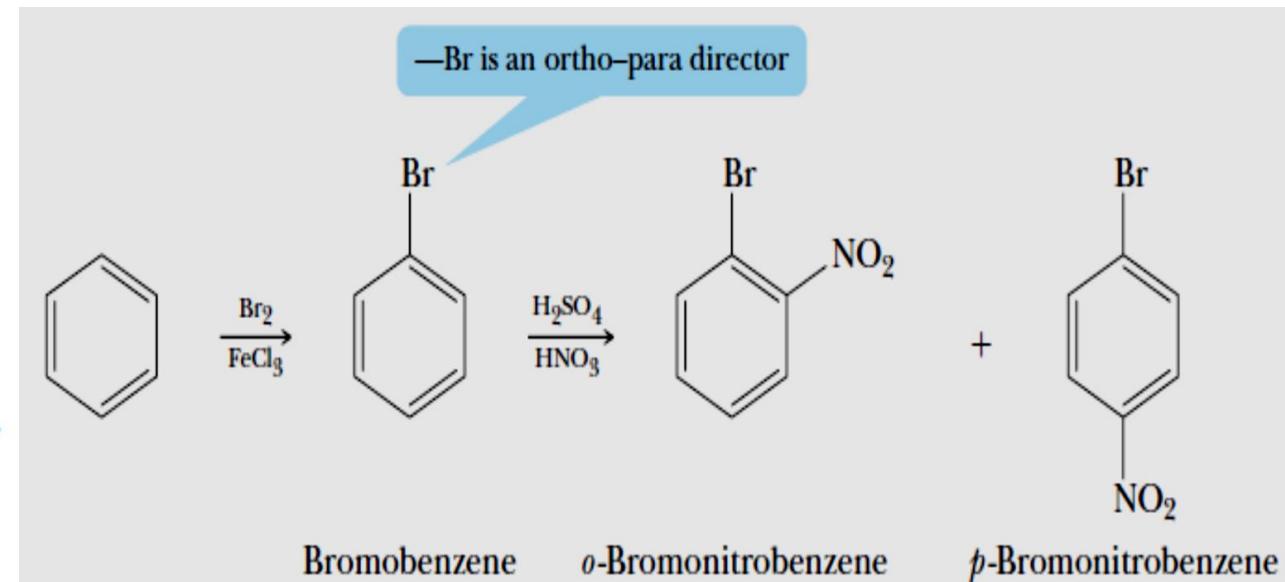
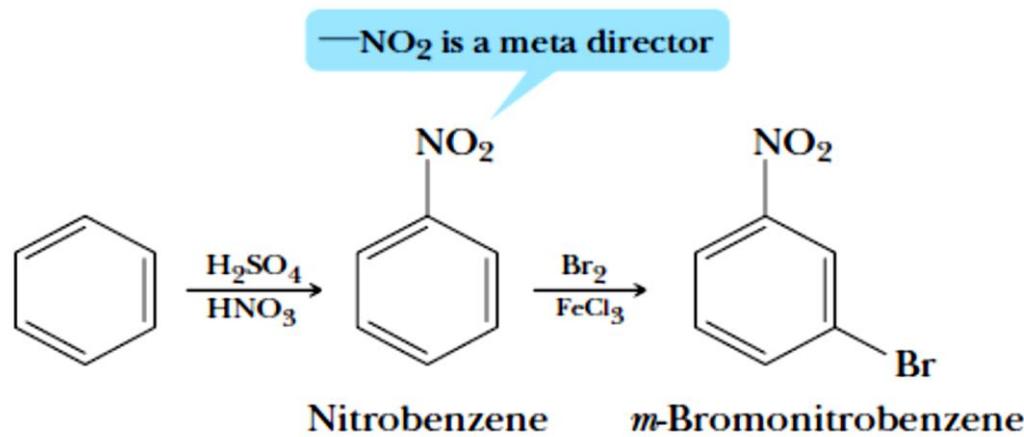
Synthesis (Preparation) of Disubstituted Benzene

1) We must consider the order in which we introduce various substituents into the ring.

For example; in the preparation of the bromonitrobenzenes:

If we nitrate first and then brominate, we will obtain the *m*-isomer.

Whereas if we brominate first and then nitrate, we will obtain a mixture of the *o*- and *p*-isomers.

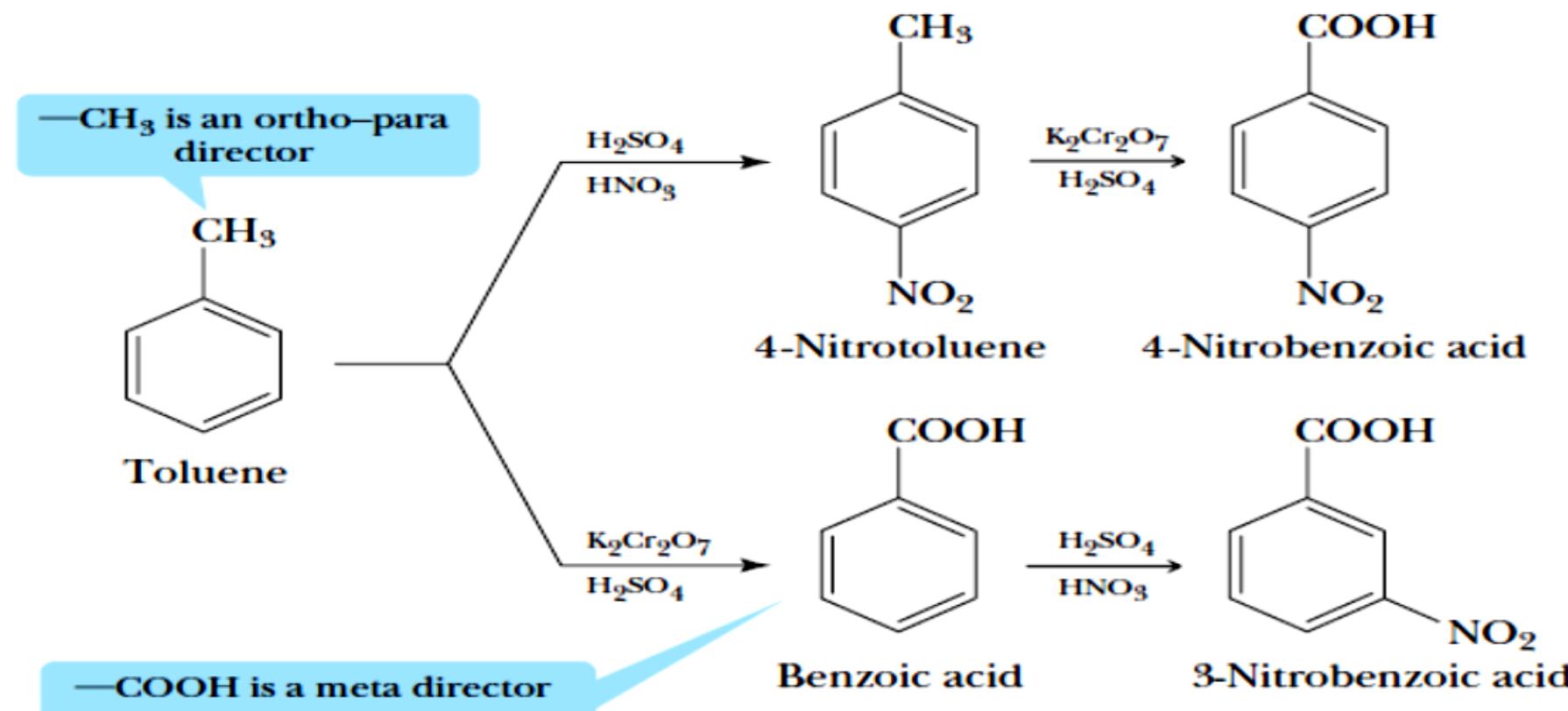


- The order in which we decide to carry out the two steps, depends upon which isomer we want.

Benzene Derivatives; Orientation and Synthesis

2) If our synthesis involves conversion of one group into another, *we must consider the proper time for this conversion.*

For example, in the preparation of nitrobenzoic acids from toluene, oxidation of a methyl group (**by $K_2Cr_2O_7$**) yields a carboxyl group ($-COOH$). The particular product obtained depends upon whether oxidation or nitration is carried out first.



Homework:

Show how to convert **toluene** to these carboxylic acids:

- 4-Chlorobenzoic acid
- 3-Chlorobenzoic acid

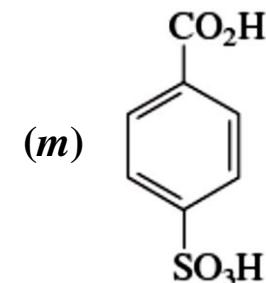
Benzene Derivatives; Orientation and Synthesis

Problem (5.2):

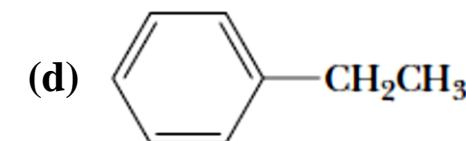
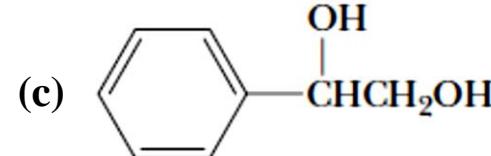
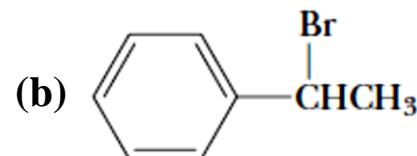
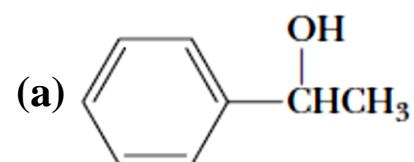
1) Write equations showing how to prepare each of the following from **benzene** or **toluene**, and any necessary organic or inorganic reagents. If an *ortho*, *para* mixture is formed in any step of your synthesis, assume that you can separate the two isomers.

- (a) *m*-Bromonitrobenzene
- (b) 1-Bromo-4-nitrobenzene
- (c) 2,4,6-Trinitrotoluene (TNT)
- (d) *m*-Bromobenzoic acid
- (e) *p*-Bromobenzoic acid
- (f) *p*-Dichlorobenzene
- (g) *m*-Nitrobenzenesulfonic acid
- (h) 1-Chloro-3-nitrobenzene

- (i) Isopropylbenzene
- (j) *p*-Isopropylbenzenesulfonic acid
- (k) 2-Bromo-2-phenylpropane
- (l) 4-*tert*-Butyl-2-nitrotoluene



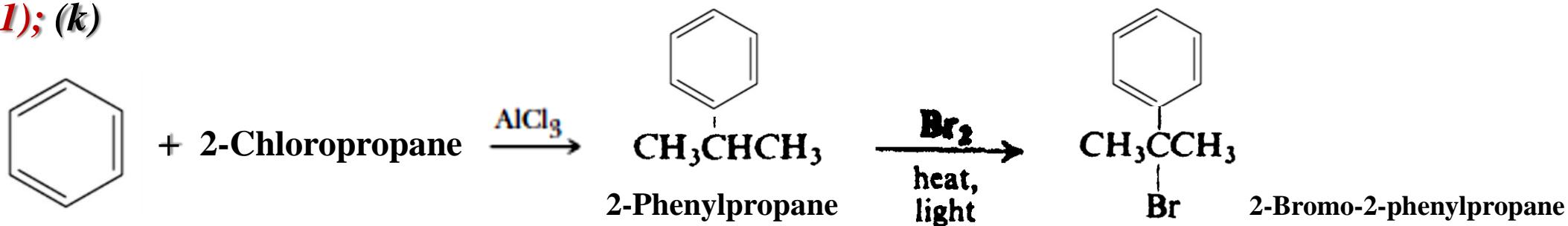
2) Using styrene, as the only aromatic starting material, and any other necessary organic or inorganic chemicals, show how to synthesize these compounds.



Benzene Derivatives; Orientation and Synthesis

Sample solutions to problem (5.2):

1); (k)



2); (a)

