Chem. 109

Organic chemistry

مذكرة نوبل للكيمياء

Nobel

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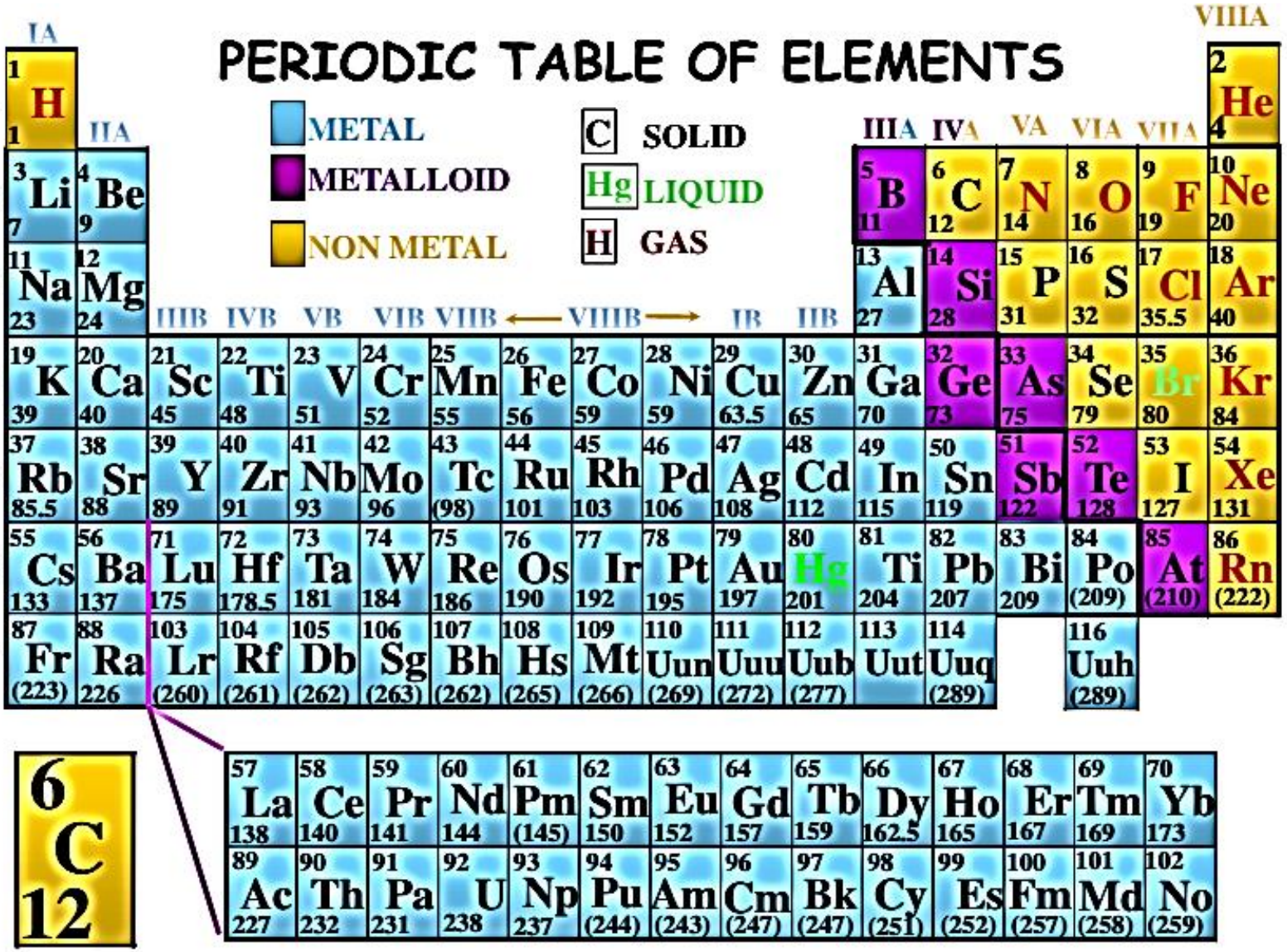
أبو عبد الرحمن



Bonding, Structural Formulas, and Molecular Shapes

Organic Chemistry

(الكيمياء العضوية)

Definition

The word Organic can be a biological or chemical term, in biology it means anything that is living or has lived. The opposite is Non-Organic.

Organic Chemistry is unique in that it deals with vast numbers of substances, both natural and synthetic.

المواد العضوية توجد طبيعية ومصنعة مثل

The clothes, the petroleum products, the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and drugs

But, from the chemical makeup of organic compounds, it was recognized that one constituent common to all was *the element carbon*.

Organic chemistry

is defined as *the study of carbon/hydrogen-containing compounds and their derivatives.*

الكيمياء العضوية : هي دراسة مركبات الكربون والهيدروجين ومشتقاتها

تدخل هذة المركبات في تركيب اعضاء الجسم المختلفة

تدخل ايضا في مجالات اقتصادية عديدة مثل الصناعة- الزراعة – الطب ومصادرها في الطبيعة البترول االفحم

	Organics	Inorganics
Bond type	**have covalent bonds (electron sharing)**	**usually have ionic bonds (electron transfer)**
Structure	**•Molecules •Nonelectrolytes**	**• Three-dimensional crystal structures • Often water-soluble, dissociating into ions -electrolytes**

	Organics	Inorganics
Melting Point & Boiling Point	–have lower melting points • Intermolecular forces broken fairly easily	–usually have higher melting points • Ionic bonds require more energy to break
Water Solubility	Nonpolar, water insoluble	Water-soluble, readily dissociate

The Uniqueness of Carbon

What is unique about the element *carbon*?

Why does it form so many compounds?

The answers lie in

The structure of the *carbon* atom.

The position of *carbon* in the periodic table.

These factors enable it to form strong bonds with

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

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

كل مركب عضوي له خصائصة الفيزيائية والكيميايةالخاصة به وهذا يعتمد على تركيب المركب .

من اسباب انتشار مركبات الكربون :-

قدرة ذرة الكربون على الارتباط ببعضها بروابط قوية مكونة سلاسل طويلة

تتحد سلاسل الكربون باشكال مختلفة قد تكون مستقيمة او متفرعة او حلقية

يمكن للكربون ان يكون روابط احادية وثنائية وثلاثية

امكانية تكوين روابط مع ذرات عناصر اخرى مثل (N –O –H)

Atomic Structure

Atoms consist of three main particles: neutrons (have no charge), protons (positively charged) and electrons (negatively charged).

تتكون الذرة من بروتونات موجبة ونيترونات متعادلة والكترونات سالبة

توجد البروتونان والنيترونات في نواة الذرة.وتوجد الالكترونات في خارج النواة موزعة في مدارات الطاقة

Neutrons and protons are found in the nucleus.

Electrons are found outside the nucleus.

Electrons are distributed around the nucleus in successive *shells* (*principal energy levels*).

Atom is electrically neutral.

i.e. Number of electrons = Number of protons

الذرة متعادلة كهربيا لان عدد البروتونات الموجبة تساوي عدد الالكترونات السالبة

Atomic number of an element is the number of protons.

العدد الذري : – هو عدد البروتونات الموجبة

The energy levels are designated by capital letters (*K, L, M, N, ..*) or whole numbers (*n*).

The maximum capacity of a shell = $2n^2$ electrons.

The maximum number of electrons in each shell = $2n^2$

No. of shell	Name of shell	Max. no. of electrons
n = 1	*K*	$2 \times 1^2 = 2$
n = 2	*L*	$2 \times 2^2 = 8$
n =3	*M*	$2 \times 3^2 = 18$
n = 4	*N*	$2 \times 4^2 = 32$

(where n = number of shell).

For example, the element carbon (atomic number 6)

6 electrons are distributed about the nucleus as

Shell	K	L	M	N
Number of electrons	2	4	0	0

Valance Electrons: Electron-Dot Structures

الكترونات التكافؤ : هي الالكترونات في مستوى الطاقة الاخير

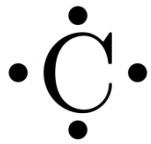
Valance Electrons are those electrons located in the *outermost energy level* (*the valance shell*).

Electron-dot structures

The symbol of the element represents the core of the atom.

The valance electrons are shown as dots around the symbol.

تكتب رمز العنصر ثم تضع نقاط حول الرمز تساوي عدد الالكترونات في مستوى الطاقة الاخير



Chemical Bonding

In 1916 G.N. Lewis pointed out that:

The noble gases were stable elements and he ascribed their lack of reactivity to their having their valence shells filled with electrons.

2 electrons in case of helium.

8 electrons for the other noble gases.

Ionic Bonds

الفلزات تحتوي على (1 أو 2 أو 3) الكترون في مستوى الطاقة الاخير فمن السهل عليها ان تفقد الكترونات المستوى الاخير حتى تصل الى التركيب الثماني او تركيب العناصر النبيلة الفلزات توجد يسار الجدول الدوري فهي تفقد الالكترونات وتتحول الى ايون موجب هذا الايون يسمى (كاتيون).

اللافلزات تحتوي على (5 أو 6 أو 7) الكترونات في مستوى الطاقة الاخير ولذلك هي تكتسب الالكترونات لتصل الي التركيب الثماني او لتركيب العاناصر النبيلة واللافلزات توجد على يمين الجدول الدوري فهي تكتسب الالكترونات وتتحول الى ايون سالب هذا الايون يسمى (انيون).

Elements at the left of the periodic table give up their valance electrons and become *+ve charged ions* (*cations*).

Elements at the right of the periodic table gain the electrons and become *-ve charged ions* (*anions*).

يحدث التجاذب بين الايون الموجب والايون السالب ويتكون الرابطة الايونية

Ionic bond

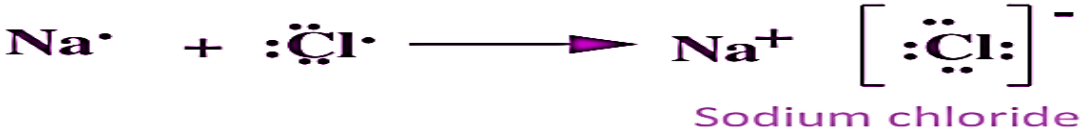
The electrostatic force of attraction between oppositely charged ions.

The majority of ionic compounds are *inorganic substances*.

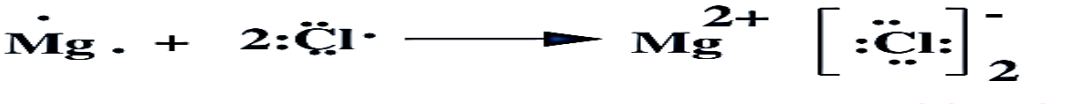
The noble gases are known for their chemical stability and existence as mono atomic molecules as they contain 8 electrons in outer most shell (valence shell) except Helium

Rn	Xe	Kr	Ar	Ne	He	Nobel gases
8	8	8	8	8	2	Valence electrons
6	5	4	3	2	1	Period no.
6	5	4	3	2	1	No. of shells

Other atoms also want electronic configurations like noble gases (concept of duplet & octet rules) due to their Stability



Sodium chloride



Magnesium chloride

Electronegativity Measures The Ability of An Atom To Attract Electrons

COVALENT BONDS

Bonds are formed between <u>two non metals</u> by sharing of one or more pairs of electrons.

CH_4, CCl_4 , O_2, H_2, H_2O, HCl, HF, NH_3, CO_2

Covalent Bonds

Elements that are close to each other in the periodic table attain the stable noble gas configuration

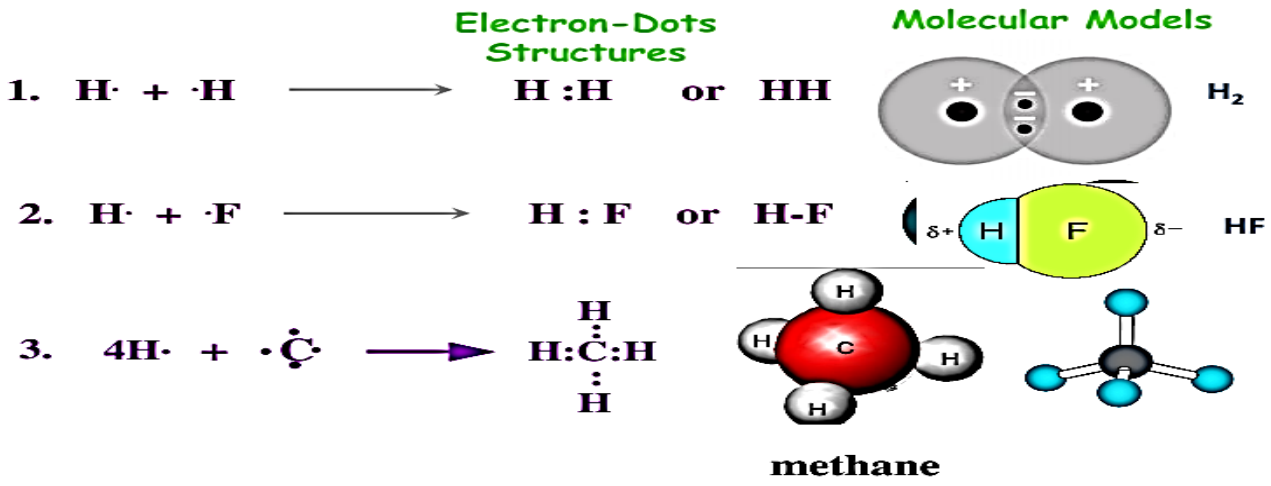
by sharing valence electrons between them.

Covalent bond

The chemical bond formed when two atoms share one pair of electrons.

A shared electron pair between two atoms or single covalent bond, will be represented by a dash (-).

Examples



In molecules that consist of two like atoms;

the bonding electrons are shared equally

(both atoms have the same electronegativity).

When two unlike atoms;

the bonding electrons are no longer shared equally (shared unequally).

A Polar Covalent Bond

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

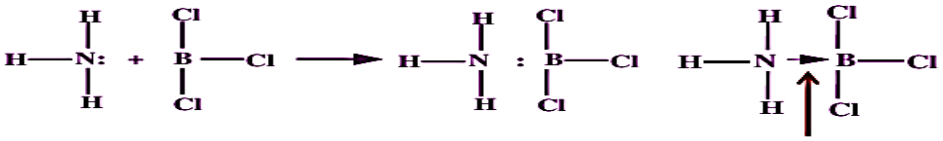
The more electronegative atom assumes a partial negative charge and the less electronegative atom assumes a partial positive charge.

Coordinate Covalent Bonds

There are molecules in which one atom supplies both electrons to another atom in the formation of a covalent bond.

Example

The reaction of boron tri chloride, BCl_3, and ammonia, NH_3.



Coordinate covalent bond.

Lewis base

The species that furnishes the electron pair to form a coordinate covalent bond.

المركب الذي يحتوي على زوج من الالكترونات الحرة

Lewis acid

The species that accepts the electron pair to complete its valance shell.

المركب الذي يستقبل زوج الالكترونات من ال base

Covalence Number — **How Many Bonds to an Atom?**

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

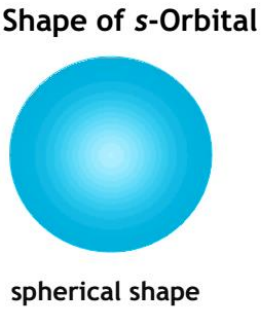
i.e. ***the covalence number is equal to the number of electrons needed to fill its valance shell.***

Shapes of Organic Molecules

Orbital Picture of Covalent Bonds

Atomic Orbitals

An atomic orbital *represents a specific region in space in which an electron is most likely to be found.*



Atomic orbitals are designated in the order in which they are filled by the letters *s, p, d,* and *f*.

Examples:

K shell has only one 1s orbital.

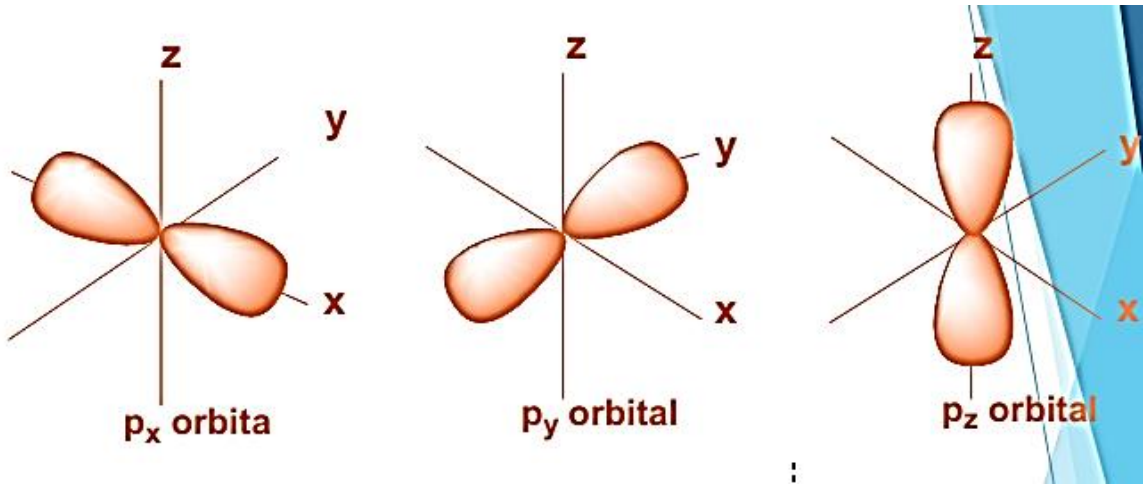
L shell has one 2s and three 2p ($2p_x$, $2p_y$ and $2p_z$).

An *s* orbital is spherically shaped electron cloud with the atom's nucleus and its center.

Atomic Orbitals

A *p* orbital is a dumbbell-shaped electron cloud with the nucleus between the two lobes.

Each *p* orbital is oriented along one of three perpendicular coordinate axes (in the *x, y,* or *z* direction).



An energy level diagram of atomic orbitals.

When filling the atomic orbitals, keep in mind that

An atomic orbital contain no more 2 electrons.

Electrons fill orbitals of lower energy first.

No orbital is filled by 2 electrons until all the orbitals of equal energy have at least one electron.

عند ملئ الاوربيتال كل اوربيتال لايحتوي على اكثر من الكترونين فقط – تملئ مستويات الطاقة الاقل طاقة اولا ثم الاعلى في الطاقة – تعبأ الاوربيتالات فرادى ثم تزدوج.

The electronic configuration of carbon (atomic number 6) can be represented as

or $1s^2 2s^2 sp^1_x 2p^1_y$

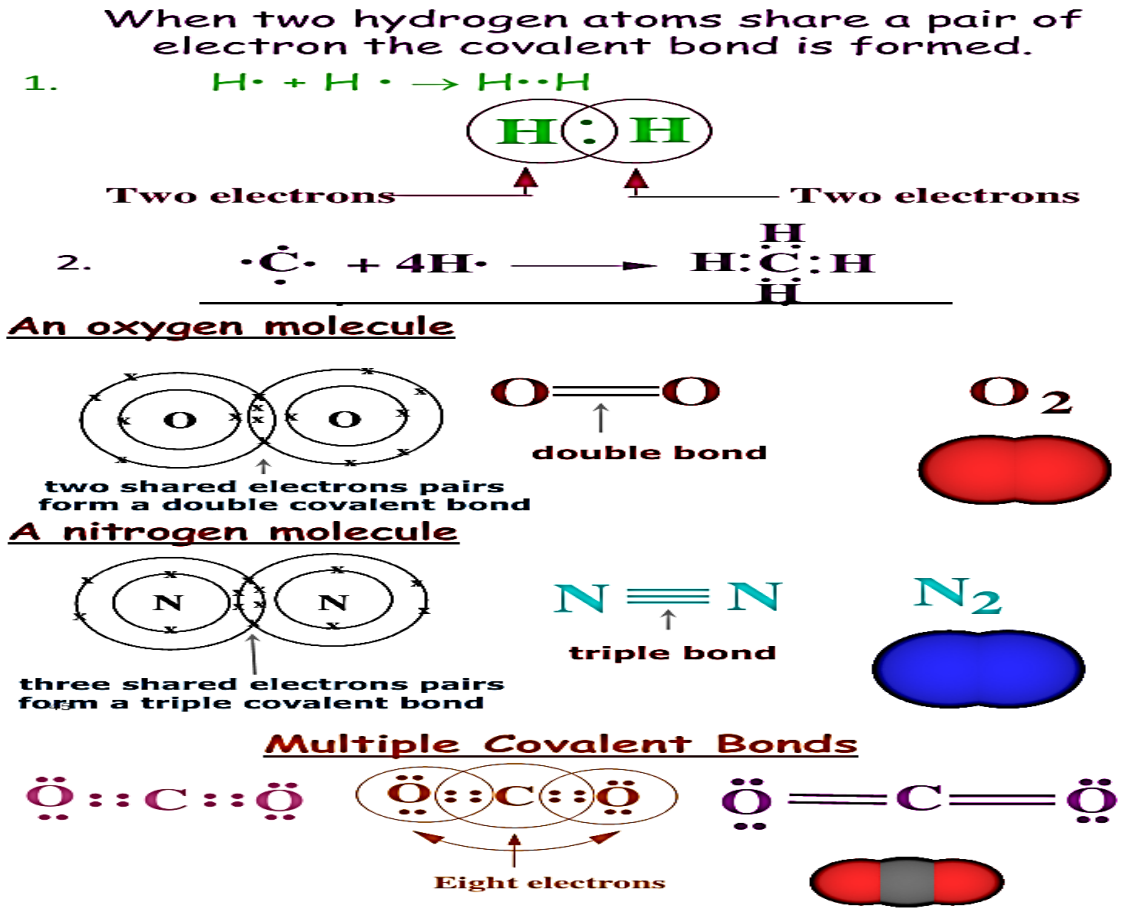
$1s^2 2s^2 2p^2$

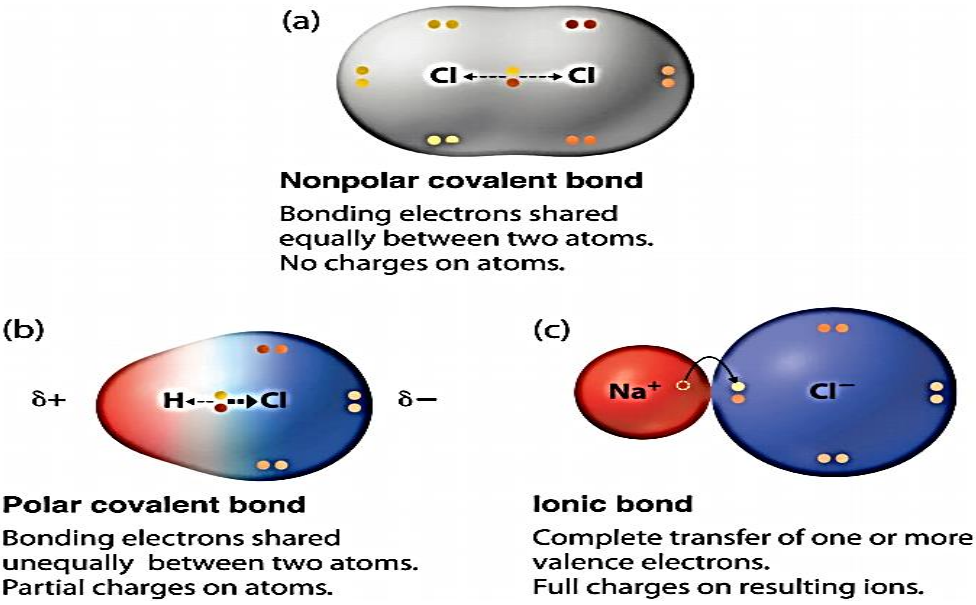
Molecular Orbitals

A covalent bond consists of the overlap between two atomic orbitals to form a molecular orbital.

تنشأ الروابط التساهمية عادة من تداخل مدارين لذرتين لتكوين جزئ

Example:





Sigma bonds (σ bonds) can be formed from

The overlap of two *s* atomic orbitals.

The end-on overlap of two *p* atomic orbitals.

تحدث الرابطة سيجما عن طريق التداخل بالرأس S-S و S-P و P- P

The overlap of two an *s* atomic orbital with a *p* atomic orbital.

pi bonds (π bonds) can be formed from the side-side overlap between two *p* atomic orbitals.

تحدث الرباطة باي عن طريق التداخل الجنب P –P فقط

Bond Energy and Bond Length

A molecule is more stable than the isolated constituent atoms.

This stability is apparent in the release of energy during the formation of the molecular bond.

الجزئ عادة اقل طاقة من الذرات المفردة بسبب فقد الطاقة اثناء تكوين الروابط

Heat of formation (bond energy)

The amount of energy released when a bond is formed.

طاقة التكوين : – هي الطاقة المنطلقة اثناء تكون الروابط.

Bond dissociation energy

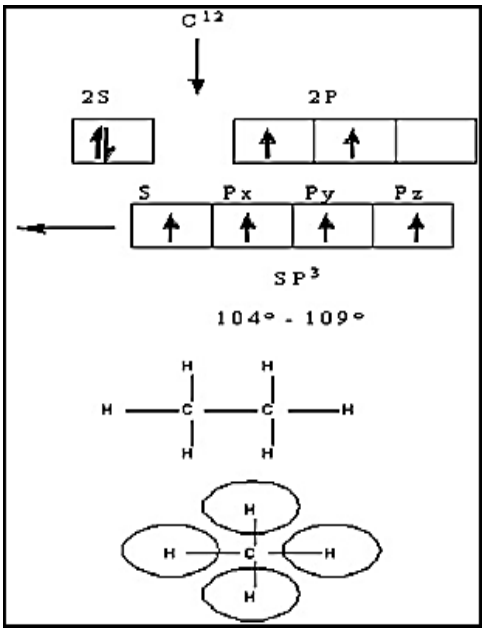
The amount of energy that must be absorbed to break a bond.

طاقة التفكك:– هي الطاقة الممتصة اثناء كسر الروابط .

Bond length

The distance between nuclei in the molecular structure.

طول الرابطة :– هي المسافة بين مركزي نواتين الذرتين .



Hybridization (Alkanes sp3)

In the case of alkanes sp^3, the three *2p* orbitals of the carbon atom are combined with its *2s* orbital to form four new orbitals called "sp^3" hybrid orbitals.

Four hybrid orbitals were required since there are four atoms attached to the central carbon atom.

These new orbitals will have an energy slightly above the *2s* orbital and below the *2p* orbitals as shown in the following illustration

Notice that no change occurred with the *1s* orbital.

التهجين في الالكان SP3

تحدث عن طريق تاخل مدار2sمع ثلاث مدارات 2pوينتج اربع اوربيتال sp3مهجنة

طاقة الاوربيتال المهجنة تكون اعلى من 2sواقل من 2p

Methane

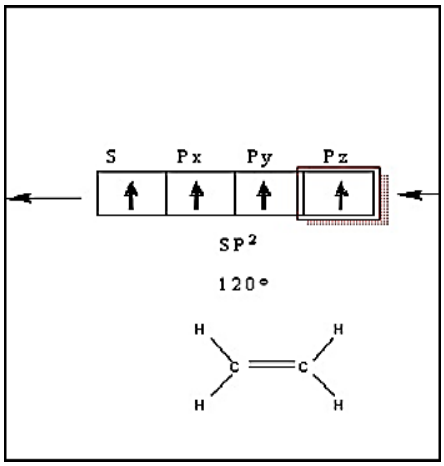
Regular tetrahedron with all H-C-H bond

angles of 109.5º.

Hybridization (Alkenes sp2)

In the case of alkenes sp^2, the *2s* orbital is combined with only two of the *2p* orbitals

(*since we only need three hybrid orbitals for the three groups. thinking of groups as atoms and non-bonding pairs*) forming three hybrid orbitals called sp^2 hybrid orbitals.



التهجين في الالكان SP2

تحدث عن طريق تاخل مدار2sمع مدارين 2pوينتج ثلاث اوربيتال sp2مهجنة

طاقة الاوربيتال المهجنة تكون اعلى من 2sواقل من 2p

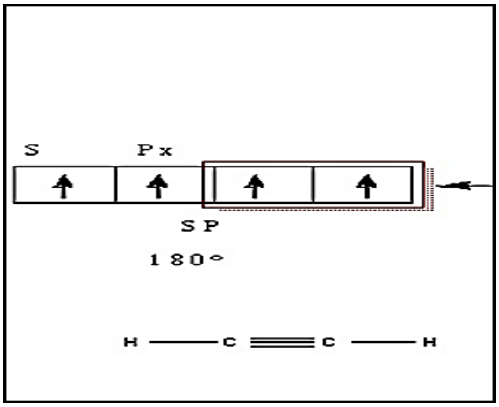
(Ethylene)

The other *p*-orbital remains unhybridized and is at right angles to the trigonal planar arrangement of the hybrid orbitals.

The trigonal planar arrangement has bond angles of 120°.

Hybridization (Alkanes sp)

In the case of alkynes *sp*, the *2s* orbital is combined with only one of the *2p* orbitals to yield two *sp* hybrid orbitals.



The two hybrid orbitals will be arranged as far apart as possible from each other with the result being a linear arrangement.
The two unhybridized *p*-orbitals stay in their respective positions (at right angles to each other) and perpendicular to the linear molecule (180°).

Inductive Effect

Inductive effect can be defined as *the permanent displacement of electrons forming a covalent bond (sigma σ bonds) towards the more electronegative element or group*.

The inductive effect is represented by the symbol, the arrow pointing towards the more electronegative element or group of elements.

(+ I) effect if the substituent electron-donating

عندما تعطي الكترونات.... ,CH3, -C2H5, -NH2, OH, OCH3 (+ I) effect

(- I) effect if the substituent electron-withdrawing

عندما تكون ساحبة للالكترونات .... (- I) effect+I): -CH3, -C2H5, -NH2, OH, OCH3,

Bond Polarity and Dipole Moment (μ)

Dipole moment (depends on the inductive effect).

A bond with the electrons shared equally between two atoms is called a nonpolar bond like in Cl-Cl and C-C bond in ethane.

عندما يكون الرابطة بين ذرتين من نفس النوع يكون الفرق في الكهروسالبية يساوي صفر وبالتالي العزم القطبي (الشد =0) ويكون المركب غير قطبي.

A bond with the electrons shared unequally between two different elements is called a polar bond.

اذا كان المركب به روابط قطبية والعزم القطبي لايساوي صفر يكون المركب قطبي polar

The bond polarity is measured by its dipole moment (μ).

Dipole moment (μ) defined to be the amount of charge separation (+δ and –δ) multiplied by the bond length.

Electronegativity of some elements

H=2.2	Li=1	Na=0.9	C=2.5	N=3	O=3.5	F=4
Mg=1.2	Al=1.5	Si=1.8	P=2.1	S=2.6	Cl=3	اكبر عنصر

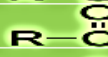
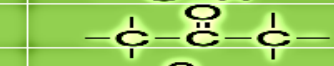
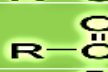
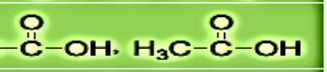
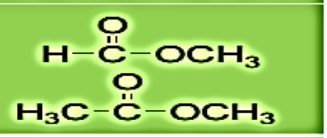
اذا كان الفرق في الكهروسالبية من صفر الى 0.3كان الرابطة تساهمية غير قطبية (non polar covalent bond) مثل H-H C2H4 CH4 N= N

اما اذا كان الفرق من 0.3الى 1.7تكون الرابطة تساهمية قطبية (polar covalent bond) مثل HCl

اذا كان الفرق اكبر من 1.7تكون الرابطة ايونية ionic bond مثل NaCl

Functional Groups

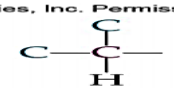
Functional Group is a reactive portion of an organic molecule, an atom, or a group of atoms that confers on the whole molecule its characteristic properties.

Class	General formula	Functional group	Specific
Alkane	RH	C – C (single bond)	H_3C-CH_3
Alkene	R – CH =	C = C	$H_2C=CH_2$
Alkyne	R—C≡CH	C≡C (triple	HC≡CH
Alkyl halide	RX	-X (X = F, Cl, Br, I)	H_3C - Cl
Alcohol	R – OH	-OH	H_3C - OH
Ether	R – O –R'	- C- O – C -	$H_3C-O-CH_3$
Aldehyde			
Ketone			
Carboxylic			
Ester			
Amine	$R-NH_2$		H_3C-NH_2

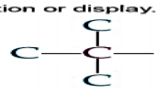
Carbon Classification

- Carbon atoms are classified according to the number of other carbon atoms to which they are attached:

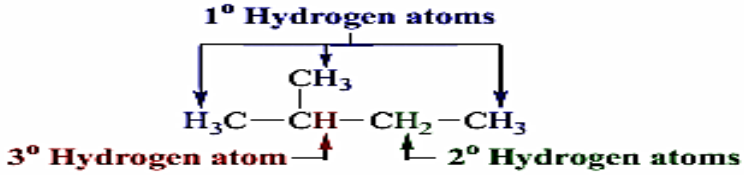
Primary (1°) carbon



Secondary (2°) carbon



Tertiary (3°) carbon



الان درب نفسك يوجد ايضا بنك اسئلة الاعوام السابقة واختبارت الميد

1	Which of the following compounds has an ionic bond?						
A	HCl	b	Br2	c	CH3F	D	LiF

2	The maximum capacity of a shell = electrons						
A	n^2	b	$4n^2$	c	$2n^2$	D	$3n^2$

3	electrons located in the *outermost energy level* (*the valance shell*).						
A	Valance Electrons	b	proton	c	Atomic no	D	Non of these

4	Elements at the left of the periodic table give up their valance electrons and become						
A	*+ve charged ions*	b	(*anions*).	c	atoms	D	electron

5	Elements at the right of the periodic table gain the electrons and become						
A	*-ve charged ions*	b	proton	c	cation	D	atom

6	*The electrostatic force of attraction between oppositely charged ions.*						
A	Non polar	b	Covalent bond	c	Ionic	D	Polar covalent

7	*The chemical bond formed when two atoms share one pair of electrons.*						
A	**Non polar**	**b**	**Ionic**	**c**	**Covalent bond**	**D**	**Polar covalent**

8	*The species that accepts the electron pair to complete its valance shell*						
A	**Lewis base**	**b**	**Lewis acid**	**c**	**Lewis carbon**	**D**	**Lewis atoms**

9	**can be formed from The overlap of two *s* atomic orbitals. The end-on overlap of two *p* atomic orbitals.**						
A	**Sigma bonds (σ bonds**	**b**	**Pi bond**	**c**	**Alpha bond**	**D**	**Hydrogen bond**

10	*The amount of energy released when a bond is formed.*						
A	***Bond length***	**b**	***Bond angle***	**c**	***Bond atoms***	**D**	***bond energy***

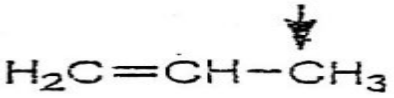
11	*The distance between nuclei in the molecular structure.*						
A	***bond energy***	**b**	***Bond length***	**c**	***Bond angle***	**D**	***Bond electrons***

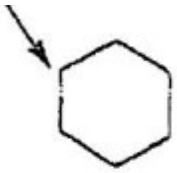
12	The trigonal planar arrangement has bond angles of						
a	140°.	b	120°.	c	180°.	D	109°.

13	.....effect if the substituent electron-donating						
A	(+ I)	b	(- I)	c	$\pm$	D	α

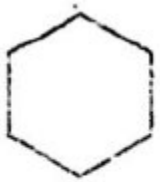
14	.....effect if the substituent electron-withdrawing						
A	$\pm$	b	(- I)	c	(+ I)	D	α

15	Which of the following compounds has an ionic bond?						
A	NaCl	b	CH_4	c	C_2H_6	D	C_2H_2

16	The type of hybridization of selected carbon is 						
A	SP^1	b	SP^2	c	SP^4	D	SP^3

17	The type of hybridization of selected carbon is 						
A	SP^1	b	SP^2	c	SP^3	d	SP^4

18	The angle ----------in linear carbon atom						
A	120°	b	180°	c	109°	d	160°

19	how many sigma bond in this comound ? 						
A	6	b	16	c	12	d	18

Key answer

السؤال	الاجابة	السؤال	الاجابة
1	D	11	B
2	C	12	B
3	A	13	A
4	A	14	B
5	A	15	A
6	C	16	D
7	C	17	C
8	B	18	B
9	A	19	D
10	D	20	– – –

CHAPTER 2

ALIPHATIC HYDROCARBON

Hydrocarbons are Organic Compounds, which contain only the two elements carbon and hydrogen.

الهيدروكربونات هي مركبات عضوية تحتوي على عنصري الكربون والهيدروجين.

Aliphatic hydrocarbons are subdivided into:

1 Saturated hydrocarbons

هيدروكربونات مشبعة اي جميع روابها احادية مثل الالكان

Alkanes; C_nH_{2n+2} (*contain carbon-carbon single bond*)

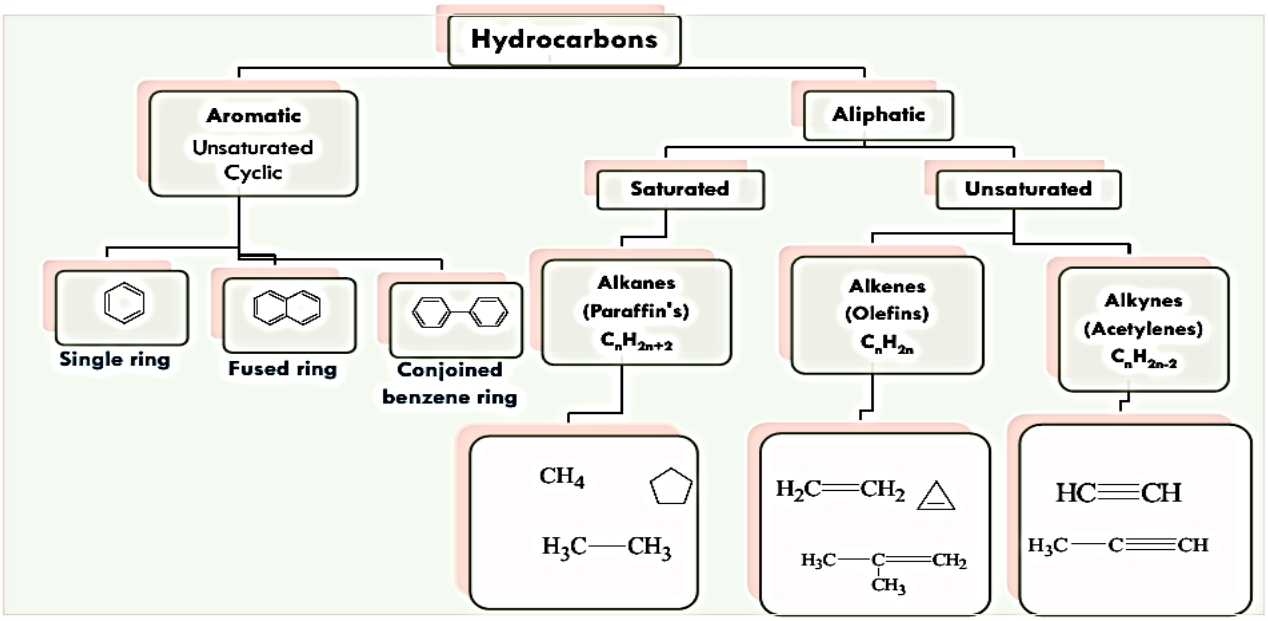
Cycloalkanes: C_nH_{2n} (*contain carbon-carbon single bond in a single ring*)

2Unsaturated hydrocarbons

هيدروكربونات غير مشبعة اي تحتوي على روابط ثنائية او ثلاثية مثل الالكين والالكاين

Alkenes : C_nH_{2n} (contain *carbon-carbon double bond)*

Alkynes *: Cn H2n-2* (contain *carbon-carbon triple bond)*



Alkanes

General formula is CnH2n+2

In alkanes, the <u>four sp3 orbitals</u> of carbon repel each other into <u>a TETRAHEDRAL</u> arrangement with <u>bond angles of 109.5º</u> like in CH4.

<u>Each sp3 orbital</u> in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.

Names, Molecular formulas and Number of Isomers of the first ten Alkanes

Name	Molecular Formula	Number of isomers
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18
Nonane	C_9H_{20}	35
Decane	$C_{10}H_{22}$	75

Structural Isomerism

Isomers are different compounds with identical molecular formulas.

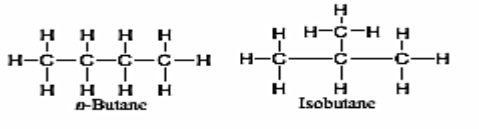
The phenomenon is called isomerism.

Structural or constitutional isomers are isomers which differ in the sequence of atoms bonded to each other.

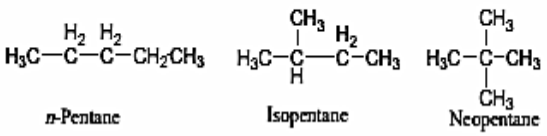
النظائر مركبات لها نفس الصيغة الجزيئية وكل تختلف فقط في طريقة ارتباط الذرات ببعضها

Examples

<u>Butanes, C_4H_{10}.</u>



➢ Pentanes, C_5H_{12}.



Alkyl Groups

An alkyl group is an alkane from which a hydrogen has been removed.

General formula CnH2n+1.

Alky group is represented by R.

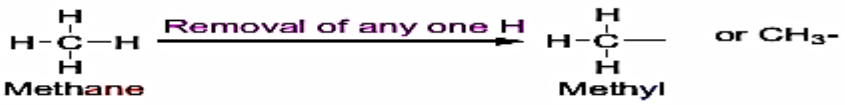
Nomenclature of alkyl groups by replacing the suffix – ane of the parent alkane by –yl.

i.e. Alkane – ane + yl = Alkyl

مجموعة الالكيل هي الكان منزوع منه ذرة هيدروجين واحدة اي صيغتة CnH2n+1 وهي عادة تكون فروع للمركبات ويرمز لها ب R

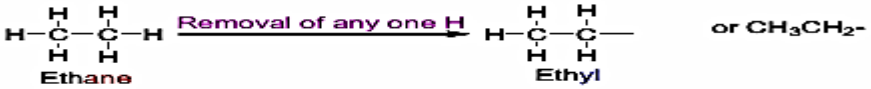
نفس اسم الالكان لكن نستبدل المقطع ane بالمقطع yl

- **Examples:**
  - ***Methane***



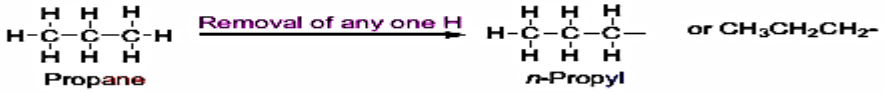
CH_3- (Methane – ane + yl) = methyl

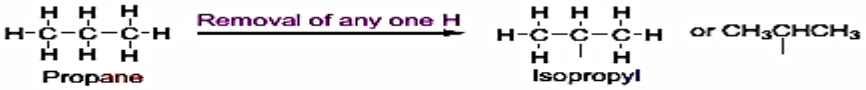
  - ***Ethane***



CH_3CH_2- (Ethane – ane + yl) = ethyl

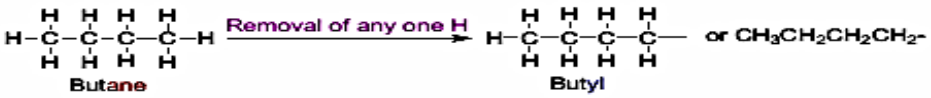
  - ***Propane***

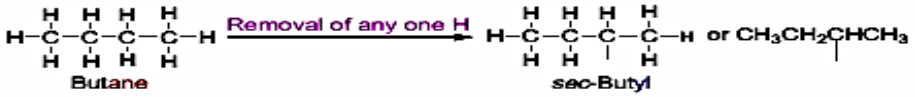


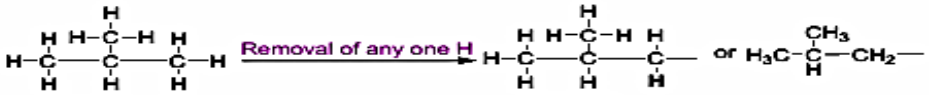


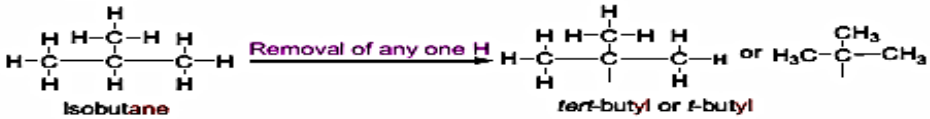
Propane – ane + yl = *n*-propyl or isopropyl

  - ***Butane***









Alkane		Alkyl Group	Abbreviation
$CH_3—H$ Methane	becomes	$CH_3—$ Methyl	Me–
$CH_3CH_2—H$ Ethane	becomes	$CH_3CH_2—$ Ethyl	Et–
$CH_3CH_2CH_2—H$ Propane	becomes	$CH_3CH_2CH_2—$ Propyl	Pr–
$CH_3CH_2CH_2CH_2—H$ Butane	becomes	$CH_3CH_2CH_2CH_2—$ Butyl	Bu–

Nomenclature

التسمية :- يوجد نوعين من التسمية وهما تسمية شائعة (اسم شهرة) وتسمية نظامية طبقا لنظام الايوباك

The older unsystematic names, (*Common names*).

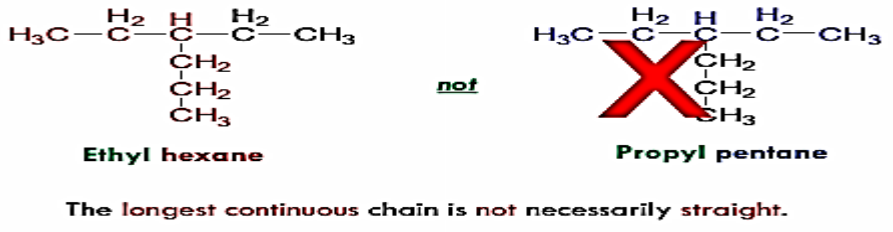
The IUPAC names.

International Union of Pure & Applied Chemistry

The IUPAC Rules قواعد الايوباك

اولا :-اطول سلسلة ممكنة – ليس شرط ان تكون مستقيمة

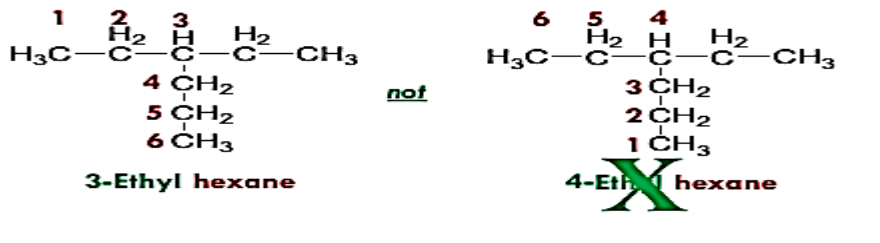
Select the parent structure *the longest continuous chain*

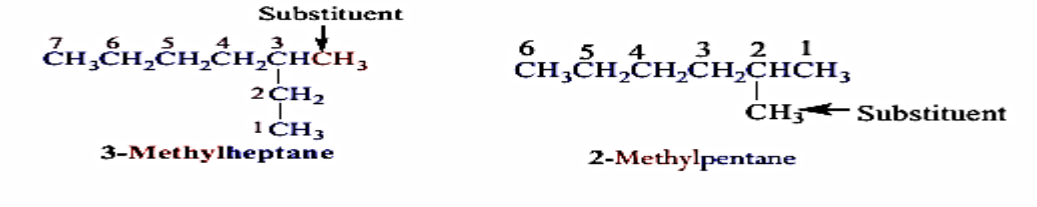


Number the carbons in the parent chain

starting from the end which gives the lowest number for the substituent

ثانيا:- الترقيم يكون من الطرف الذي يعطي التفرع اقل رقم ممكن





To name the compound;

The position of the substituent on the parent carbon chain by a number.

The number is followed by a hyphen (-).

The combined name of the substituent (ethyl).

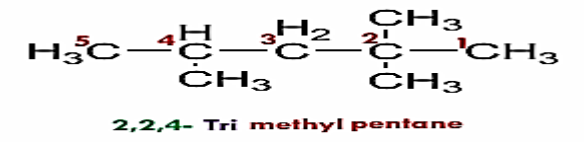
The parent carbon chain (hexane)

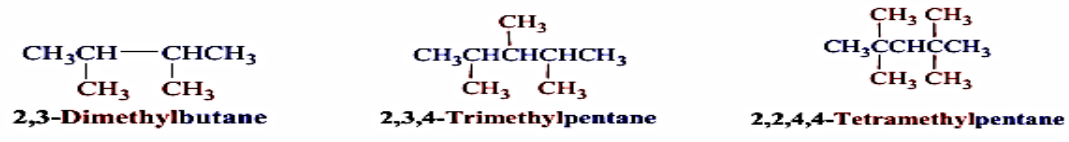
If the same alkyl substituent occurs more than once on the parent carbon chain,

the prefixes di-, tri-, tetra-, penta-, and so on

are used to indicate two, three, four, five, and so on.

في حالة تكرار نفس الفرع او مجموعة الالكيل نستخدم di-, tri-, tetra-, penta على حسب عدد التكرار ونستخدم ايضا الارقام لتحديد موضع الارتباط

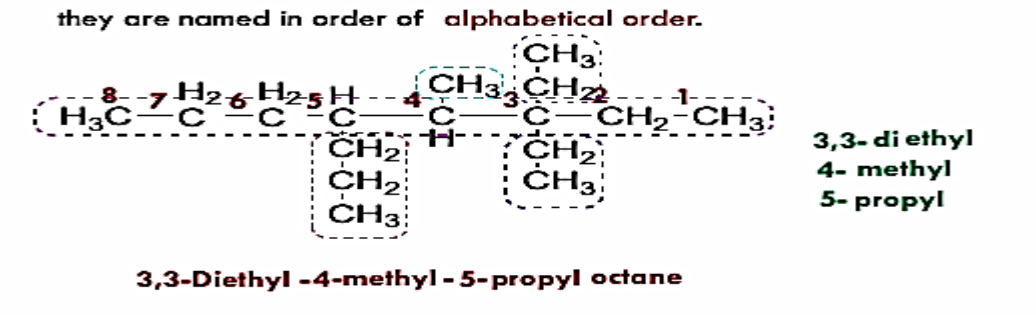




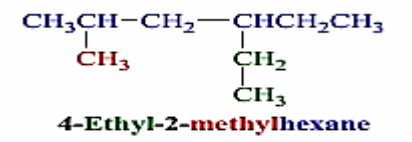
If different alkyl substituents are attached on the parent carbon chain,

they are named in order of alphabetical order.

رابعا :- اذا كان هناك اكثر من فرع نرتب على حسب الابجدية

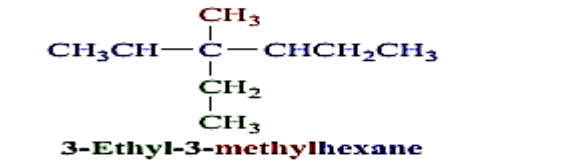


Note that each substituent is given a number corresponding to its location on the longest chain. The substituent groups are listed alphabetically.



When two substituent are present on the same carbon, use the number twice.

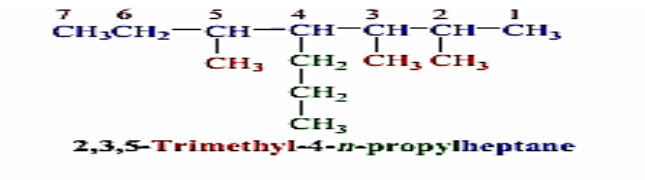
خامسا :- عند وجود تفرعين عند نفس الكربون نكرر الرقم مرتين .



When two chains of equal length compete for selection as the parent chain,

choose the chain with the greater number of substituents.

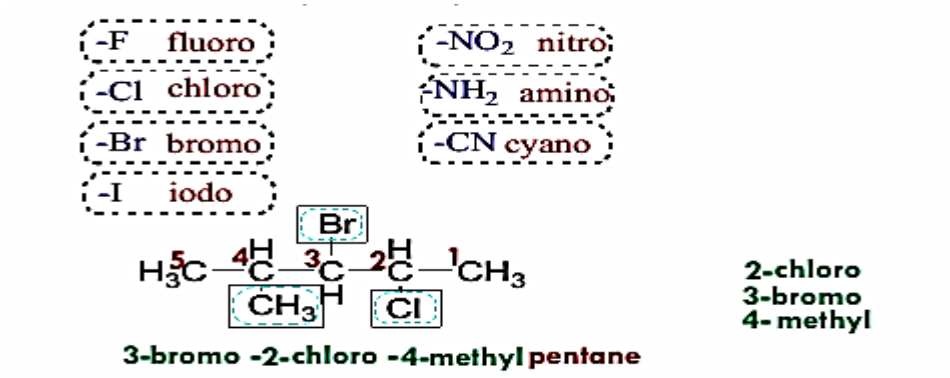
سادسا :- في حالة تساوي طولي سلستين نختار السلسة التي تحتوي على اكبر عدد من النفرعات.



If substituents other than alky groups are also presents on the parent carbon chain;

all substituents are named alphabetically.

سابعا :- عند وجود فروع اخرى غير مجموعة الالكيل ترتب جميع الفروع ابجديا .



The two principal sources of alkanes are petroleum and natural gas.

Petroleum and natural gas constitute the chief sources of

Alkanes up to 40 Carbons

Aromatic

Alicyclic (Cyclic aliphtic hydrocarbons)

Heterocyclic

Physical Properties of Alkanes, Alkenes and Alkynes

Physical States

C1 (C2) to C4 are gases,

C5 to C17 are liquids,

C18 and larger alkanes are wax –like solids.

Solubility

Alkanes, Alkenes and Alkynes are nonpolar compounds.

Their solubility " Like dissolve like"

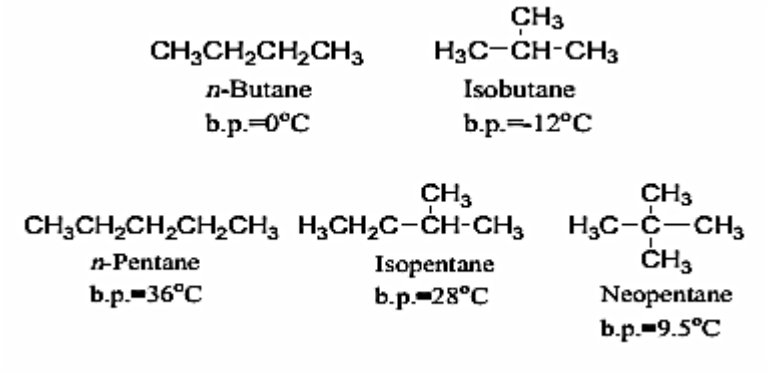
Alkanes, Alkenes and Alkynes are soluble in the nonpolar solvents;

carbon tetrachloride, CCl_4 and benzene,

الالكان والالكين والالكاين جميعهم غيرقطبي ولذلك يذوب في المذيبان الغير قطبية مثل البنزين ورابع كلوريد الكربون . ولا يذوب في الماء (لان الماء مركب قطبي)

Alkanes, Alkenes and Alkynes are insoluble in polar solvents like water.

C. Boiling Points



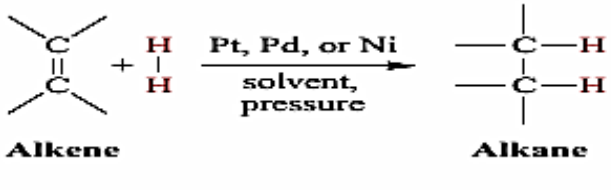
كلما زاد التفرع قلت درجة الغليان وكلما زاد الوزن الجزيئئ زادت درجة الغليان

- Boiling point decreases with increasing branches
- Boiling point increases with increasing molecular weight.

Preparation of Alkanes

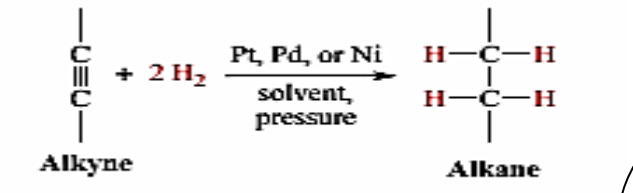
تحضير الالكانات

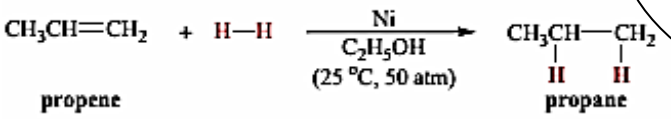
Hydrogenation of Alkenes and Alkynes



تكسر الرابطة الثائية
ويتم اضافة ذرتين
هيدروجين مكان الرابطة

باستخدام Pt , Pd, Ni

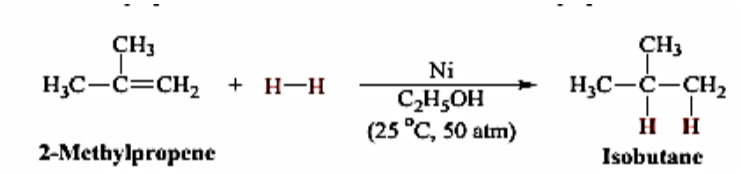




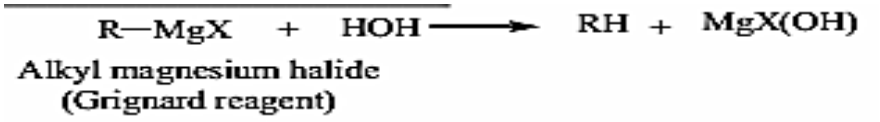
Grignard reagent is alkyl magnisum halied

قرينارد يضيف R

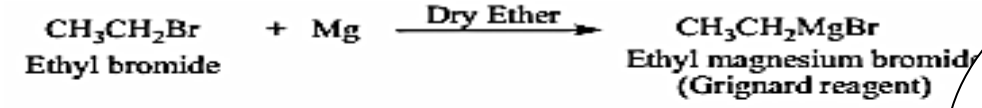
وتتبع بعملية إضافة ماء دائما ويخرج Mg x
ويضاف ال R (OH)

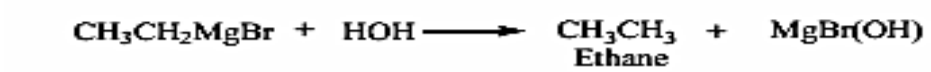


2) Hydrolysis of Grignard Reagent



Grignard reagents **react readily with any source of protons to give hydrocarbons.**

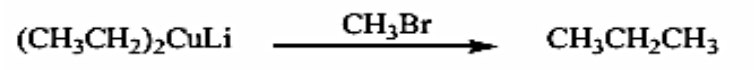




Cuprate في هذا التفاعل يخرج Li مع Br

و R تظل مع Cu و ال R الثانية تخرج مع ال CH3 ويتكون الالكان .

By coupling of alkyl halides with dialkyl cuprate (all kinds of alkanes)

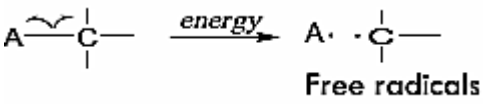


Notations for bond breaking and bond making

A covalent bond can be broken in either two ways,

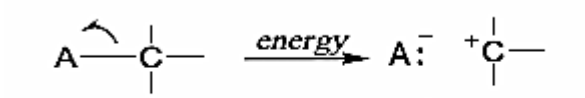
كسر الروابط نوعان :- كسر متجانس ويتكون منه شقوق حرة اي عكس تكوين الرابطة التساهمية فكل ذرة تأخذ الالكترون التى شاركة به

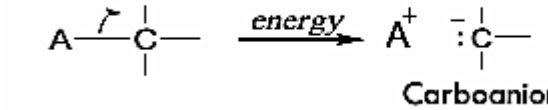
Homolytic cleavage.



Heterolytic cleavage.

النوع الثاني هو كسر غير متجانس وفية يتم الكسر لكن الذرة ذات الكهروسالبية الاعلى تظل محتفظة بزوج الالكترونات الموجودين في الرابطة وتحمل شحنة جزيية سالبة والذرة الاقل في الكهروسالبية تحمل شحنة جزيئية موجبة .





Reactions of Alkanes

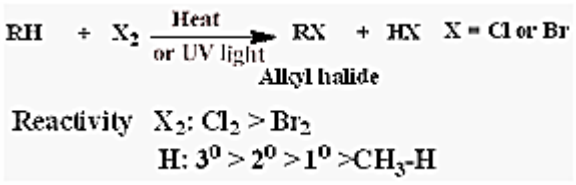
تفاعلات الالكانات

Saturated hydrocarbons undergo very few reactions, so they are called Paraffinic hydrocarbons. (Latin *parum*, little; *affinis*, affinity)

Halogenation

تفاعلات الهلجنة

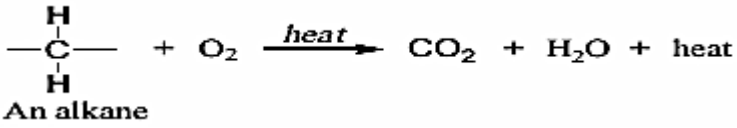
The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed



في تفاعل الهلجنة يتم إضافة 2x واحدة
تأخذ Hوتخرج والثانية تحل محل ال H

ال xيكون كلور او فلو او بروم لكن اليود ضعيف جدا

Combustion



تفاعلات احتراق الهيدروكربونات

ينتج دائما عنها CO2 و H2O .

Halogenation

Substitution reaction of alkanes,

i.e. replacement of hydrogen by halogen,

usually chlorine or bromine, giving alkyl chloride or alkyl bromide.

Flourine reacts explosively with alkanes

It is unsuitable reagent for the preparation of the alkyl flourides.

Iodine is too unreactive

It is not used in the halogentaion of alkanes.

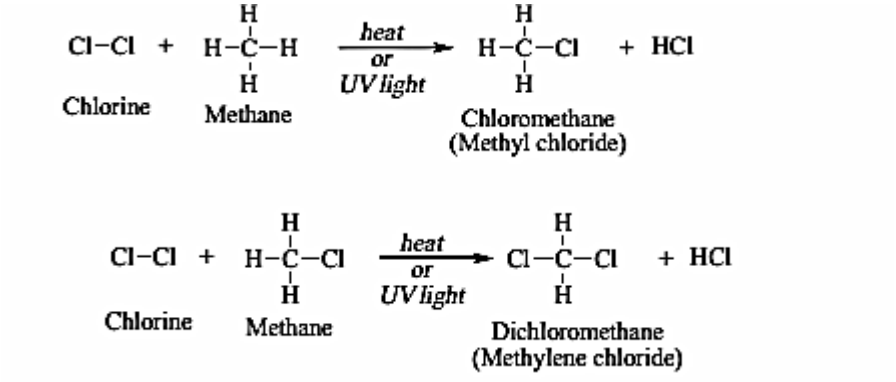
Halogenation of alkanes take place at

high temperatures or under the influence of ultraviolet light

الهلجنة تحدث عند درجات حرارة مرتفعة او اشعة فوق بنفسجية

Halogenation

Chlorination of an alkane usually gives a mixture of products



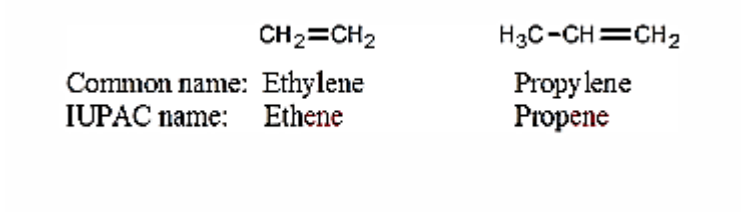
2 ALKENES

Alkenes are hydrocarbons that contain a *carbon–carbon double bond*.

Alkenes are also *Olefins*.

General formula is C_nH_{2n}

The simplest members of the Alkenes series are C_2 & C_3



The Structure of Alkenes

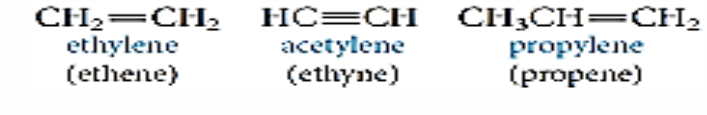
Hybridization; *sp^2*-hybridized orbitals

The angle between them is 120° and bond length C=C (1.34 Å).

A trigonal planar.

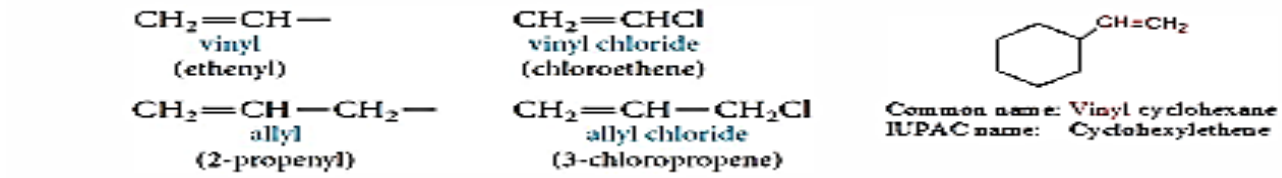
Common Names

The simplest members of the alkene and alkyne series are frequently referred to by their older common names, ethylene, acetylene, and propylene.



Two important groups also have common names; They are the vinyl and allyl groups.

These groups are used in common names.



Nomenclature of Alkenes

The IUPAC rules for naming alkenes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

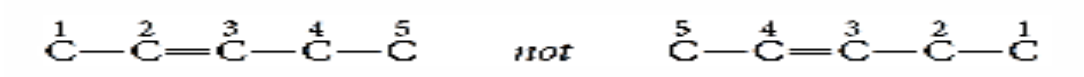
The ending *-ene* is used to designate a carbon–carbon double bond.

Select the longest chain that includes *both carbons of the double bond*.

نختار اطول سلسلة تحتوي على الرابطة الثائية يستبدل المقطع ane بالمقطع ene

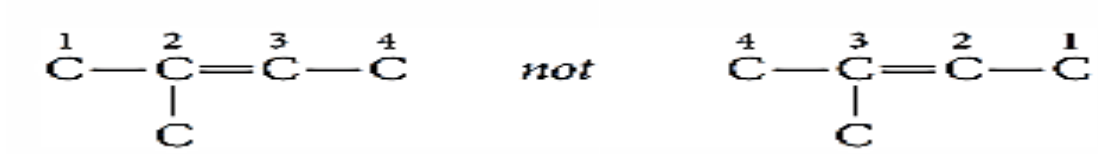
Number the chain from the end nearest the double bond so that the carbon atoms in that bond have the lowest possible numbers.

نرقم من الطرف الاقرب للرابطة الثنائية



If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.

اذا تساوى الترقيم من الطرفين نختار الطرف الاقرب للتفرع



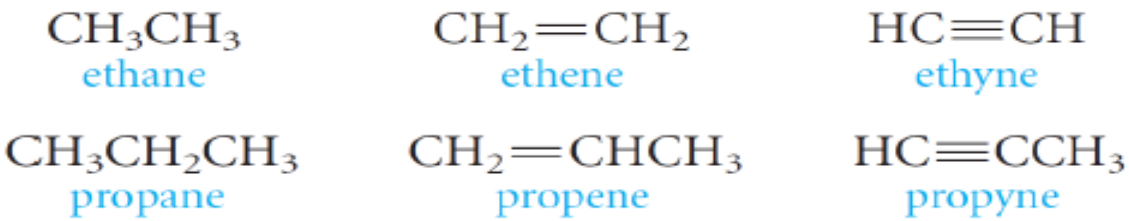
Indicate the position of the multiple bond using the *lower numbered carbon atom* of that bond.

نحدد رقم الرابطة الثائية بالرقم الاقل التى تقع عنده الرابطة

The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane, -ene,* or *-yne*) tells us whether the bonds are single, double, or triple.

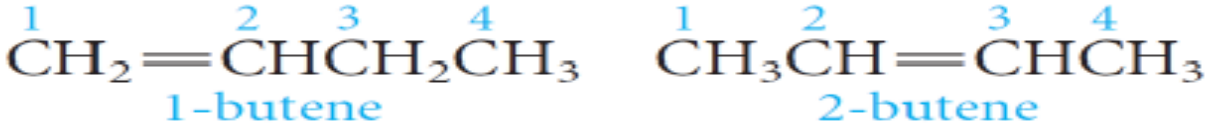
No number is necessary in these cases, because in each instance, only one structure is possible.

في بعض الاحيان ليس من الضروري كتابة ارقام (لانه لايوجد الا شكل واحد ممكن للمركب) وهذا في حالة وجود ذرتين او ثلاثة كربون فقط.



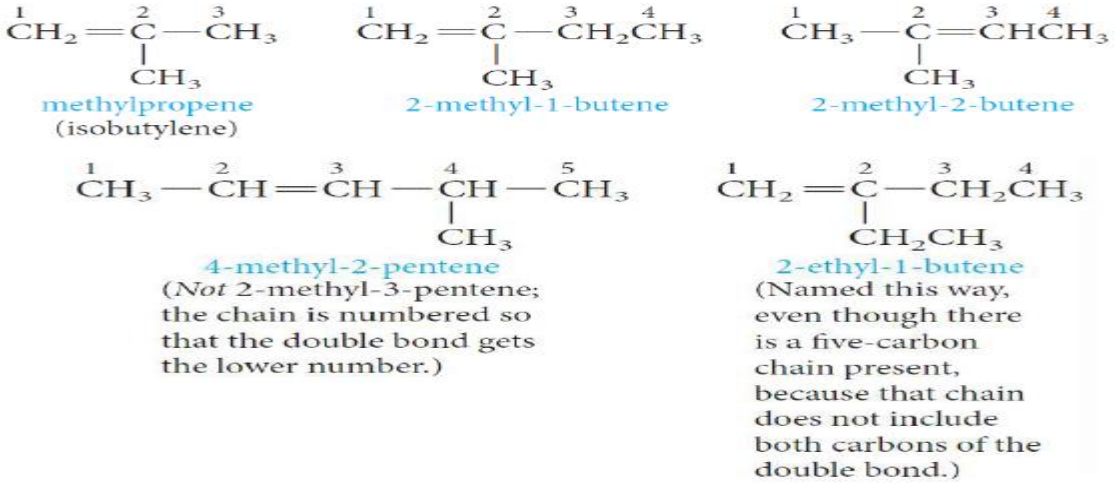
With four carbons, a number is necessary to locate the double bond.

اما في حالة وجود اكثر من ثلاث ذرات كربون لابد من ذكر رقم يدل على موضع الرابطة الثائية.



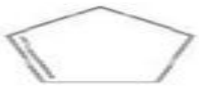
Branches are named in the usual way.

وايضا في الالكين ترقم الفروع

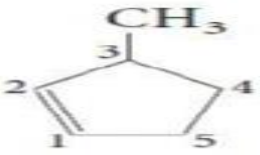


With cyclic hydrocarbons, we start numbering the ring with the carbons of the double bond.

في حالة الالكين الحلقي نبدأ الترقيم من عند الرابطة الثنائية.



cyclopentene
(No number is necessary, because there is only one possible structure.)



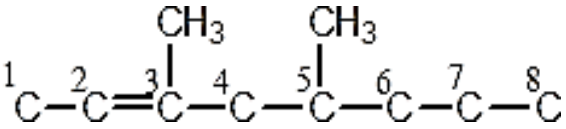
3-methylcyclopentene
(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)

Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

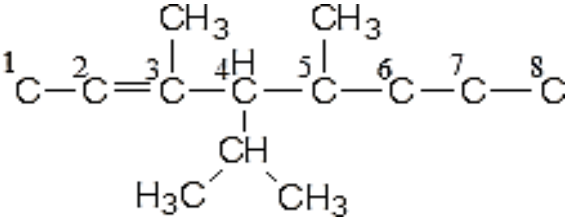
The parent carbon chain is an Octene.

The double bond is located between the 2nd and 3rd carbons

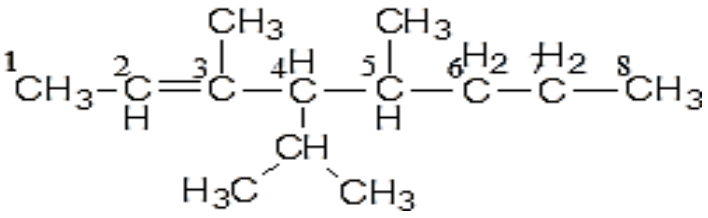
Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



An isopropyl group is attached on carbon 4.

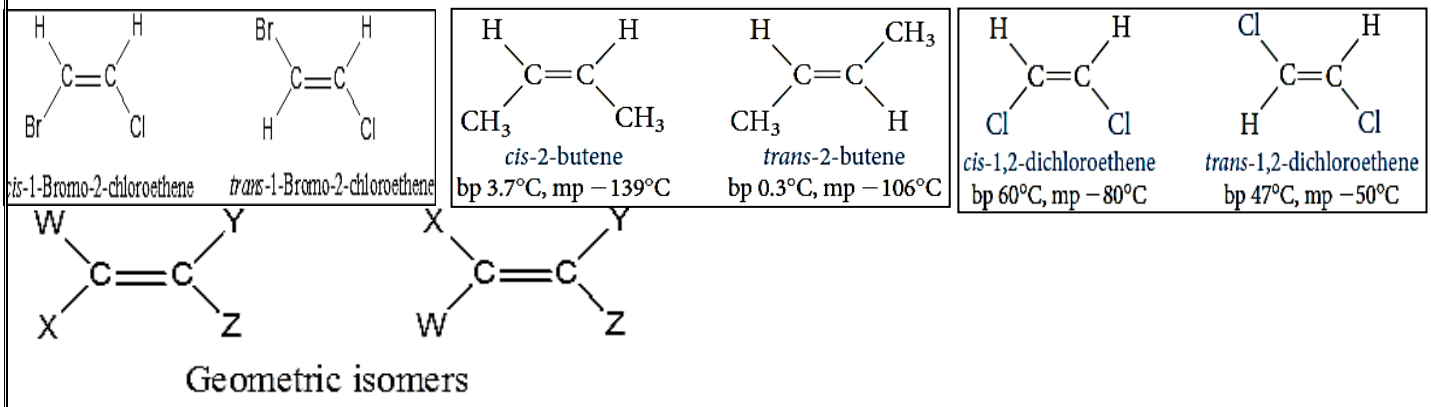


Put the missing hydrogens to get the correct structure.



Geometric Isomerism in Alkenes

In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.



when W differs from X and Y from Z, Alkenes exist as geometric isomers

***cis* isomer; when two similar groups are on the same side of the double bond.**

سيس :- عندما تكون المجوعات في نفس الجهة من الرابطة الثائية.

***trans* isomer; when two similar groups are on the opposite sides of the double bond.**

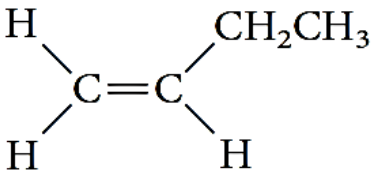
ترانس :- عندما تكون المجوعات في جهتين مختلفتين من الرابطة الثائية .

They have different physical properties and can be separated by fractional crystallization or distillation.

If (W = X or Y = Z), geometric isomerism is not possible.

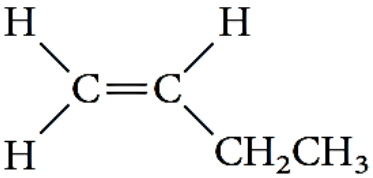
اذا ارتبطت ذرة الكربون الموجودة بالرابطة الثنائية بنفس الذرة او نس المجموعة في هذة الحالة

(no geometrical isomerism)اي لايوجد تشكل هندسي ولا سيس ولا ترانس

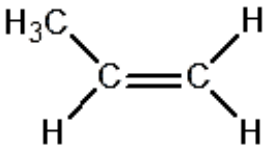


1-butene

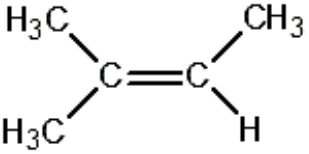
is identical to



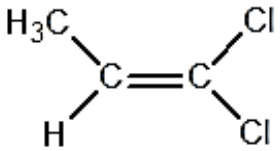
1-butene



Propene



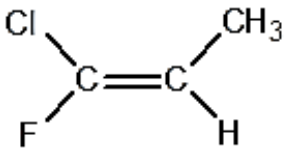
2-Methyl-2-butene



1,1-Dichloropropene

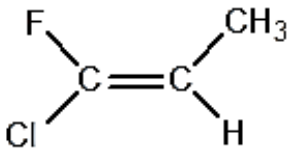
For alkenes with four different substituent such as

في حالة وجود اربع مجموعات مختلفة حول الرابطة الثنائية نستخدم في هذة الحالة E , Zبدل من سيس وترانس



(I)

or



(II)

Another system, the *E, Z* system,

Basically, the E,Z system works as follows;

Arrange the groups on each carbon of the C=C bond in order of priority

The priority depends on atomic number:

اولا نرتب المجموعات حول الرابطة الثنائية على حسب العدد الذري لاول ذرة مرتبطة بالرابطة الثانئية الذرة الاعلى في العدد الذري لها الاولوية.

The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

Thus, in structure (I),

Cl > F, and CH_3 > H.

If the two groups of higher priority are on the same side of the C=C plane,

***The* isomer is labeled *Z;* (from the German *zusammen,* together).**

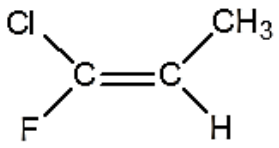
نحدد المجموعة او الذرة الاكثر اولوية ثم نقارنها بالجهة الاخرى من الرابطة اذا كان مقابل للمجموعة الاكبر (اي تشبة السيس اذا هي Z)

اما اذا كانت المجوعة الاعلى اولوية مقابلة للمجموعة او الذرة الاصغر في الجهة الاخرى من الرابطة (اي تشبة ترانس اذا هي E).

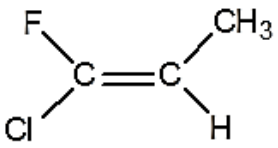
If the two groups of higher priority are on opposite sides of the C=C plane,

The isomer is labeled E; (from the German entgegen, opposite).

Priority: Cl > F, CH_3 > H

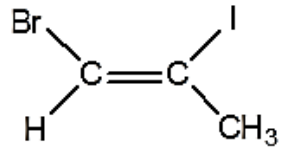


Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)



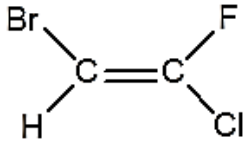
E-1-Chloro-1-fluoropropene
(Cl and CH_3 on opposite side)

Priority: Br > H, I > CH_3



Z-1-Bromo-2-iodopropene

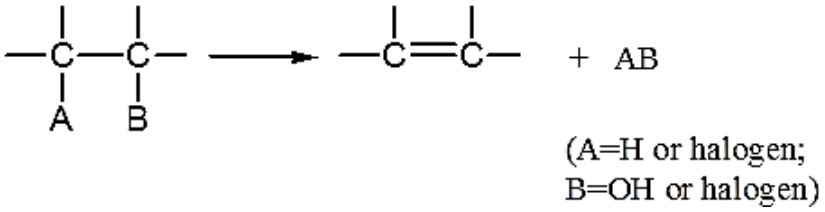
Priority: Br > H, Cl > F



E-1-Brfomo-2-chloro-2-fluoroethene

Preparation of Alkenes

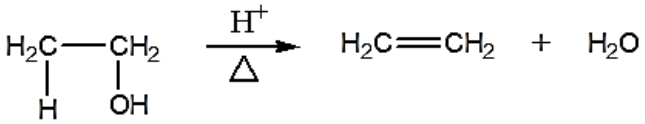
Alkenes are prepared by *Elimination* of an atom or group of atoms from adjacent carbons to form *carbon-carbon double bond*.



Dehydration of Alcohols

نزع الماء من الكحولات

When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.



IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

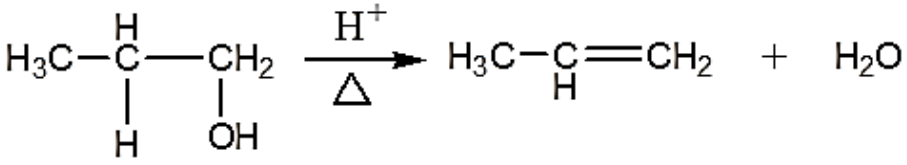
يتم نزع الماء عن طريق حمض الكبريتيك اوحمض الفوسفوريك

اي ينزع H و OH و يتكون مكانهم رابطة ثنائية

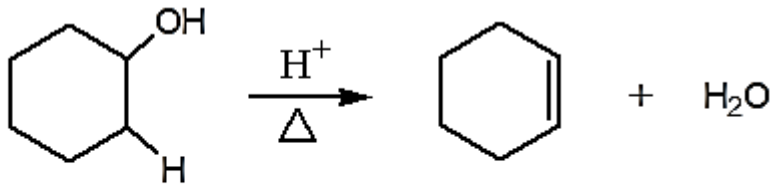
The acid *catalysts* most commonly used are sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.

Dehydration of Alcohols

Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as H_2SO4 or H_3PO_4



IUPAC name:	1-Propanol	Propene
Common name:	*n*-Propyl alcohol	Propylene



IUPAC name: Cyclohexanol Cyclohexene
Common name: Cyclohexyl alcohol

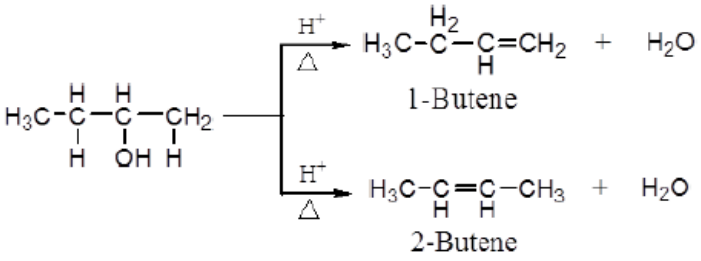
Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: the dehydration of 2-butanol.

عند نزع الماء طبقا لقاعدة سيتزيف يتم نزع الOH و لكن H تنزع من ذرة الكربون الفقيرة بالهيدروجين (يوجد عندها عدد اقل من ذرات الهيدروجين وهذا هو major product

alkyl substituents attached to C=C)



Saytzeff's Rule applies

In every instance in which more than one Alkene can be formed

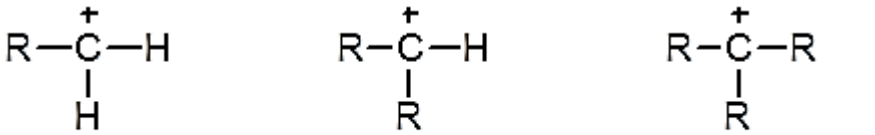
The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

Classes of Carbocations

ذرة الكربون الاولية مرتبطة ب Rواحدة

ذرة الكربون الثانوية مرتبطة ب 2R

ذرة الكربون الثلاثية مرتبطة ب 3R



1° carbocation 2° carbocation 3° carbocation

The ease of formation and the stabilities of carbocations follow the order

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

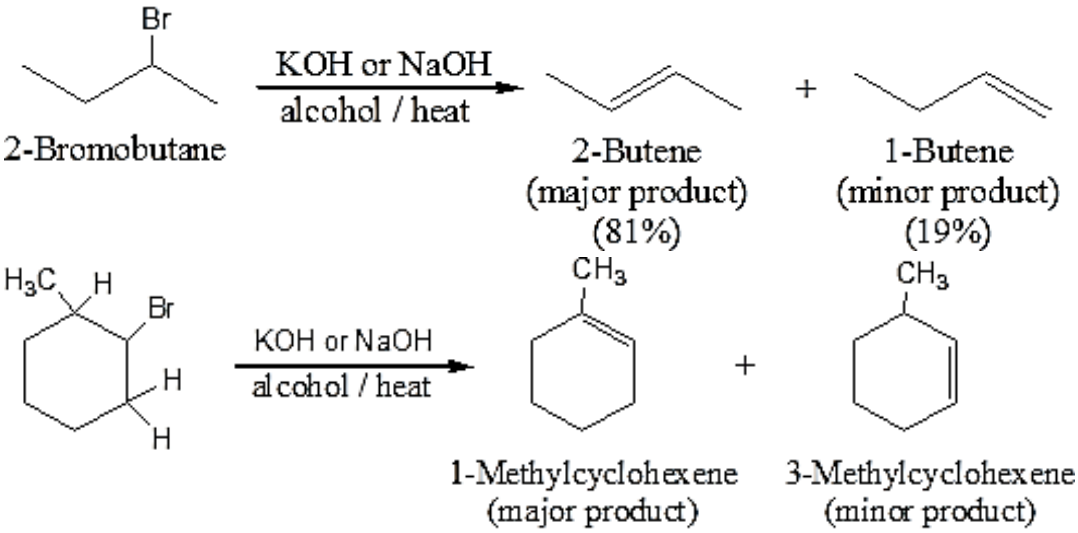
Ease of formation and stabilities of carbocations

Dehydrohalogenation of Alkyl Halides

نزع الماء من هاليد الالكيل في وجود قاعدة قوية مثل (KOH,NaOH)

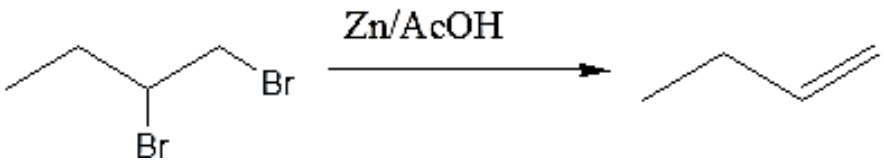
Alkenes can also be prepared under alkaline conditions.

heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.



Dehalogenation of Vicinal Dibromides

نزع الماء من ائي برومو فينيلVicinal Dibromides في وجود Zn/AcOH



يتم نزع 2xباستخدام الزنك والخل

ويتكون مكانهم رابطة ثنائية

Reactions of Alkenes

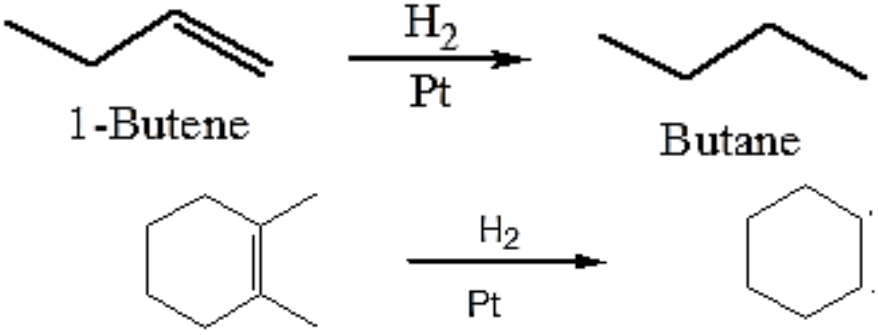
The chemistry of alkenes can be divided into two general types of reactions:

Electrophilic Addition Reactions

تفاعلات الاضافة الالكتروفيلية (وفيها يتم كسر الرابطة الثنائية والاضافة عليها).

1Addition of Hydrogen: Hydrogenation

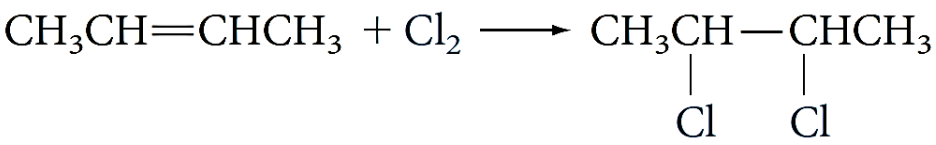
Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an Alkane.



الاضافة في الوضع cis

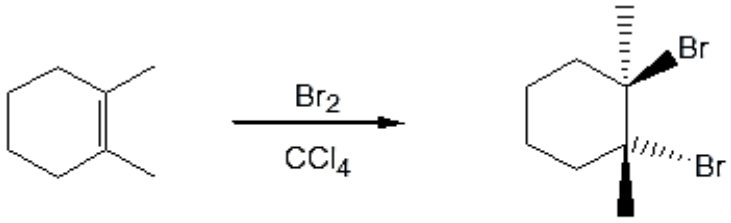
1,2-Dimethylcyclohexene *cis*-1,2-Dimethylcyclohexane

2Addition of Halogen: Halogenation



2-butene 2,3-dichlorobutane

الاضافة في الوضع trans

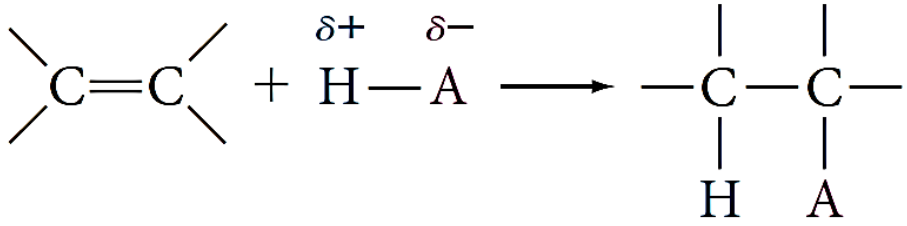


1,2-Dimethylcyclohexene *trans*-1,2-Dibromocyclohexane

Iodine is too unreactive and will not add to the double bond.

Fluorine is too reactive and reacts explosively with an alkene.

3Addition of Acids



عند اضافة الاحماض يضاف الH على احد طرفي الرابطة الثائية (الغني) الذي يحتوي عدد اكبر من الهيدروجين .

طبقا لقاعدة ماركينوكوف (الغني يزداد غنى والفقير يزداد فقر) الغني بالهيدروجين طبعا وكذلك إضافة HOH

Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), and water (H-OH).

Any electron-rich species is called a nucleophile.

<u>Examples of Electrophile</u>: - Any electron-deficient species is called an electrophile.

Positive reagents: protons (H^+), alkyl group R^+ , nitronium ion (NO_2^+), etc….

Neutral reagents having positively polarized centers: HCl, bromine (because it can be polarized so that one end is positive).

Lewis acids: molecules or ions that can accept an electron pair ⇒ BF_3 and $AlCl_3$.

Metal ions that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+}).

Examples of Nucleophile:

a)Negative ions

e.g. HO^- Hydroxide ion, HS^- Hydrosulphide ion, RO^- Alkoxide ions,

$:N\equiv C:^-$ Cyanide ion, $:\ddot{X}:^-$ Halide ions, ...etc.

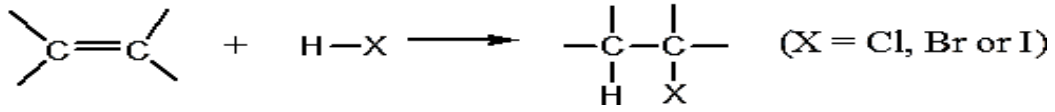
b) Neutral molecules

e.g. H_2O , $R-O-H$, $R-O-R$, H_3N , R_3N , ...etc.

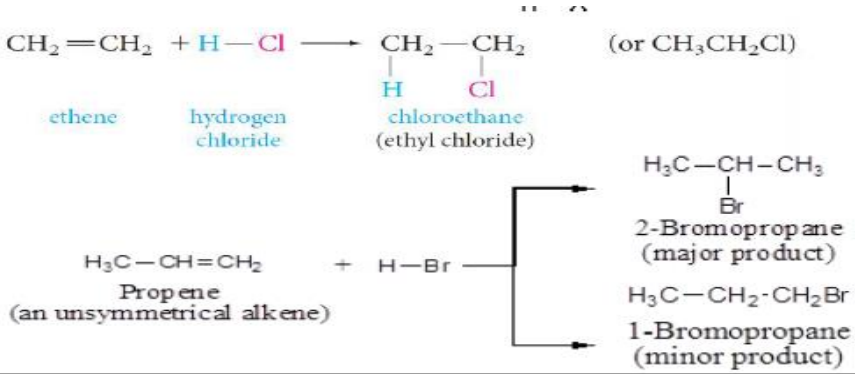
3.1. Addition of Hydrogen Halide

Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

General equation



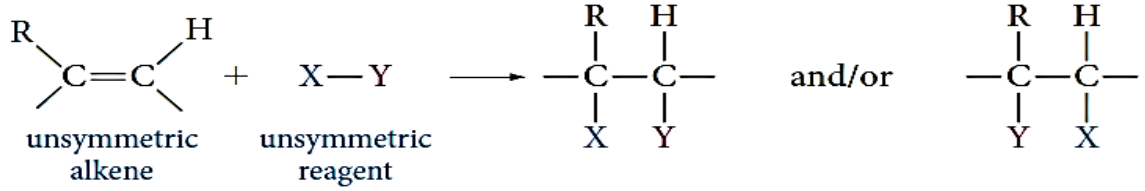
Examples;



Reagents and alkenes can be classified as either symmetric or unsymmetric with respect to addition reactions.

If a reagent and/or an alkene is symmetric, only one addition product is possible.

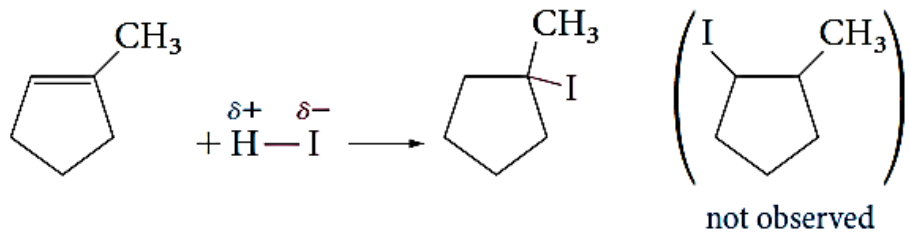
But if *both* the reagent *and* the alkene are *unsymmetric,* two products are, in principle, possible.

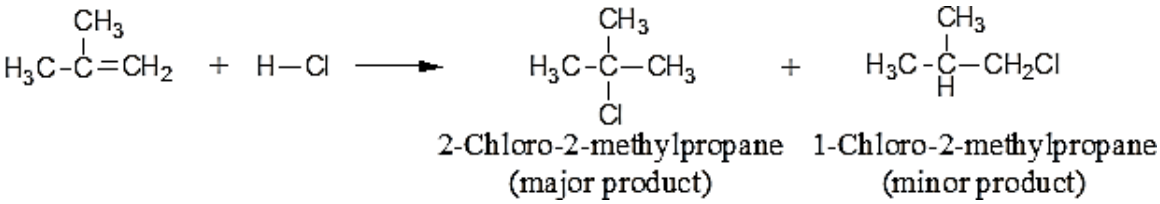


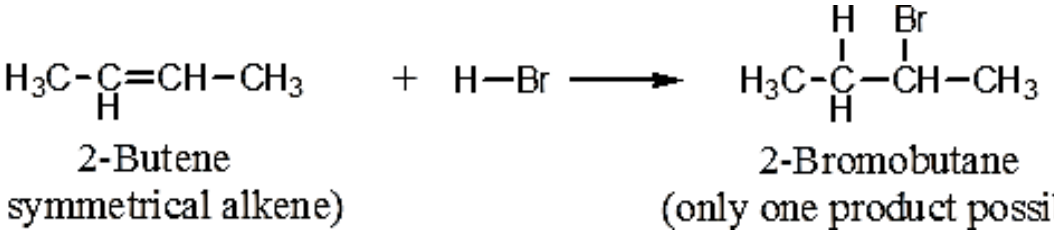
Markovnikov's Rule

In electrophilic addition of* H—X *to Unsymmetrical Alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.

الغني يزداد عنى (اي يضلف ال Hعلى الكربونة الاكثر هيدروجين ويضاف ال Xعلى الطرف الاخر اي الاقل هيدروجين)

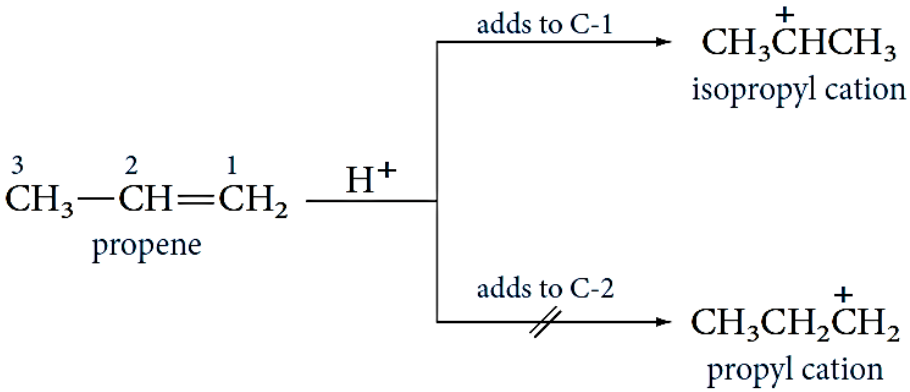






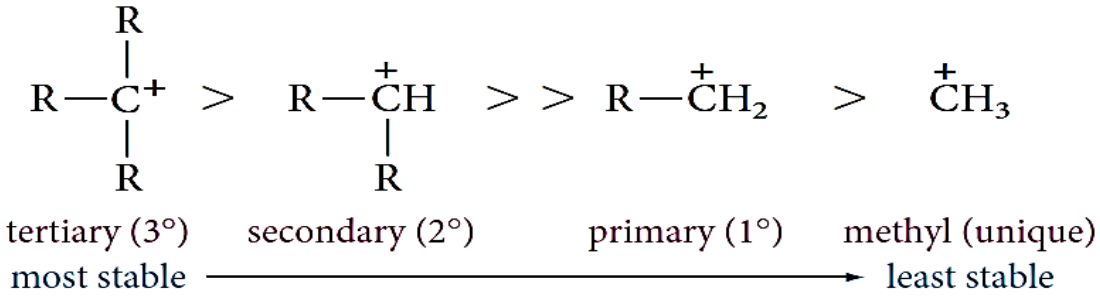
Explanation for Markovnikov's Rule

Example; Addition of HBr to propene



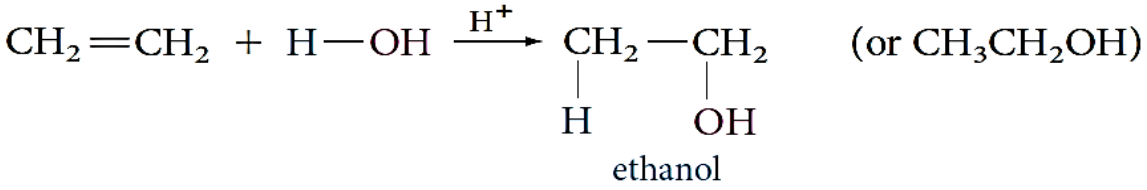
In modern terms Markovnikov's rule can be restated:

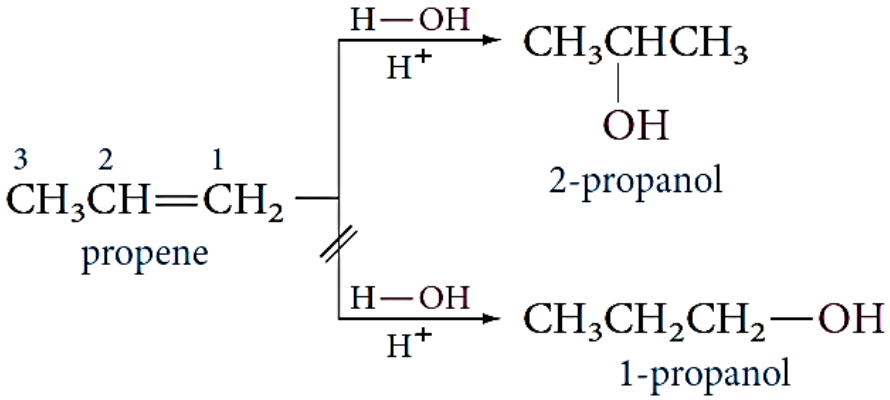
The addition of an unsymmetrical reagent* HX *to an unsymmetrical alkene proceeds in such a direction as to produce the more stable carbocation.

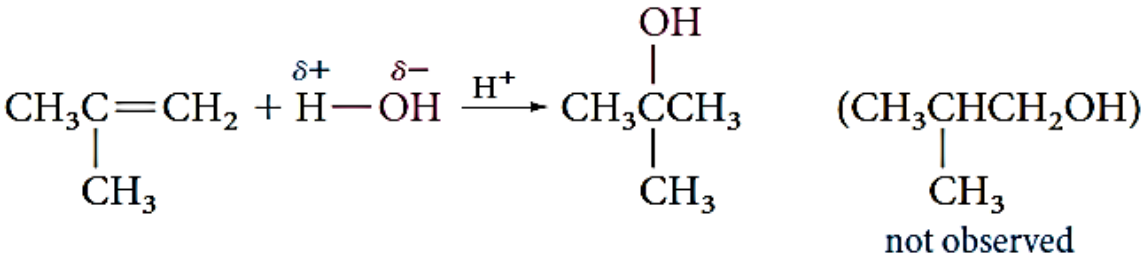


3.2. Addition of Water: Hydration

If an acid catalyst is present, water (as H-OH) adds to alkenes and the product is alcohol.

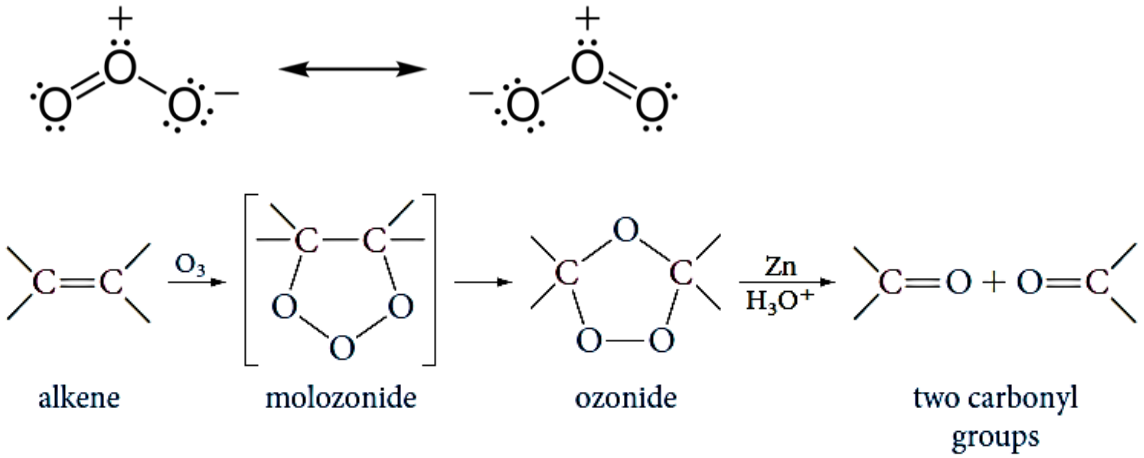






Oxidation Reactions

Ozonolysis



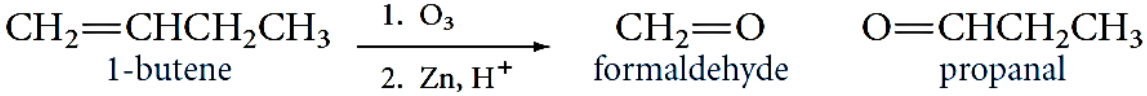
Ozonolysis

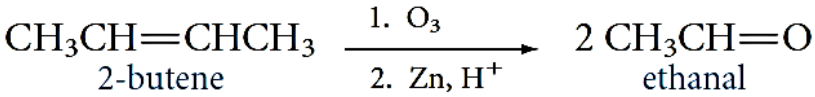
الاكسدة بالاوزون ببساطة اكسر الرابطة من النصف وضع 2O هكذا O = ثم =O
اكتب المركبين الناتجين في حالة الالكين العادي يتكون مركبين وفي الحلقي يتكون مركب

Ozonolysis can be used to locate the position of a double bond.

Example;

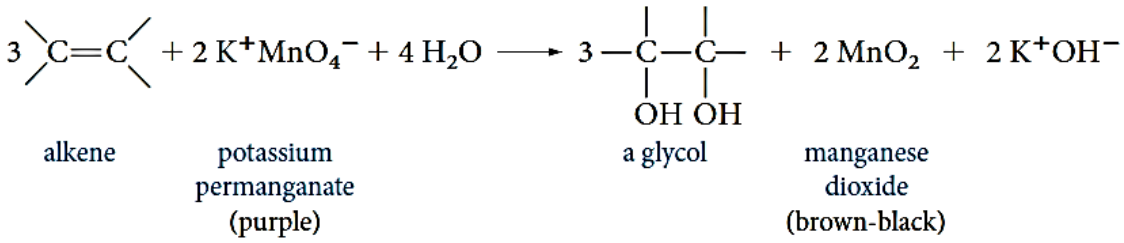
Ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.

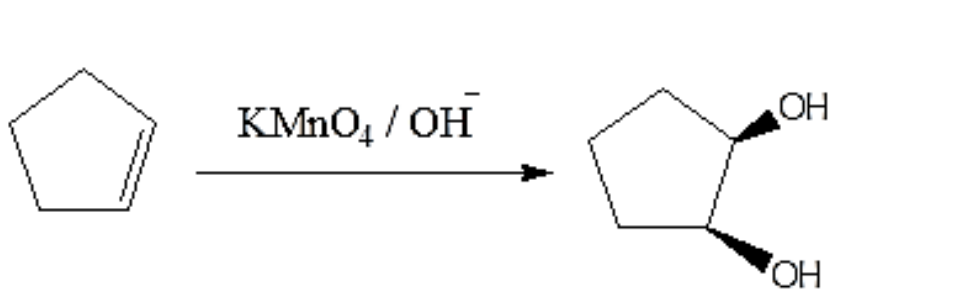




Oxidation Using $KMnO_4$

Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).





الاضافة OH 2
في الوضع cis

Cyclopentene *cis*-Cyclopentane-1,2-diol

ALKYNES

The Structure of Alkynes

Alkynes are hydrocarbons that contain a *carbon–carbon triple bond*.

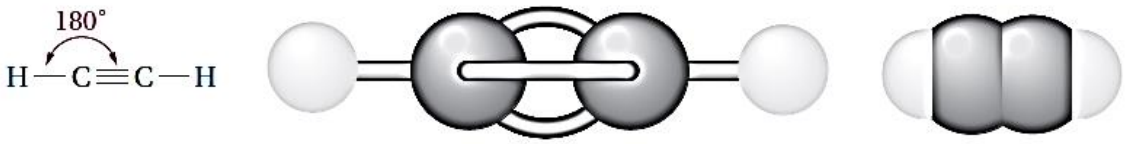
Alkynes are also known as *Acetylenes*.

General formula is C_nH_{2n-2}

Hybridization; *sp*-hybridized orbitals

The angle between them is 180° and the bond length 1.20 A°

Linear shape

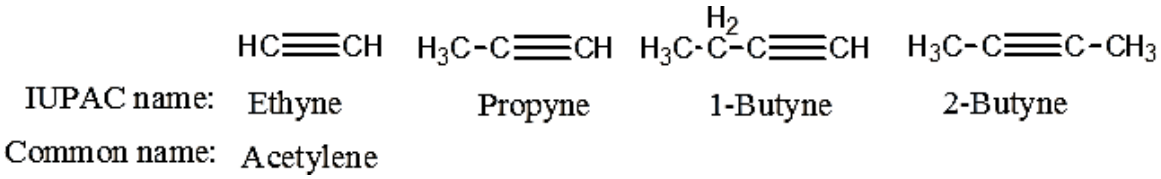


Nomenclature of Alkynes

The simplest members of the Alkenes series are C_2 & C_3

Named are derived from the corresponding alkanes by replacing the –ane ending by –yne.

IUPAC rules as discussed for Alkenes .



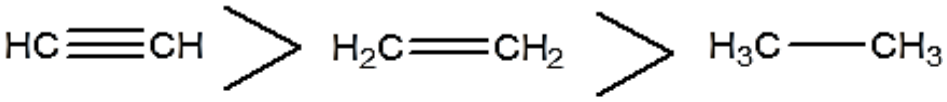
Example

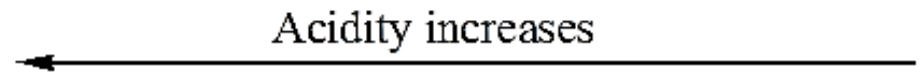
3-Chloro-2,7-dimethyl-4-nonyne

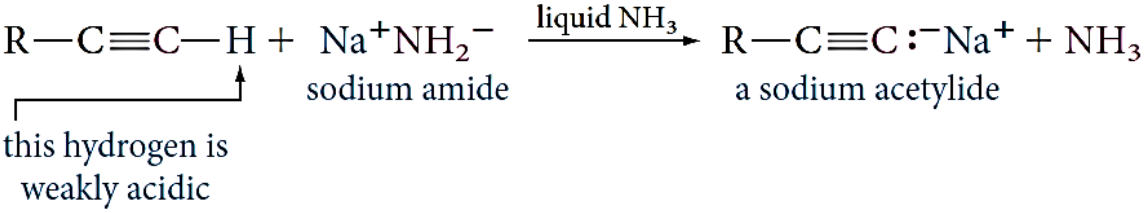
Acidity of Alkynes

A hydrogen atom on a triply bonded carbon (Terminal Alkyne) is weakly acidic and can be removed by a very strong base (as Sodium amide).

تعود حامضية الالكاين الى ال H الطرفية بجوار الرابطة الثلاثية تكون سهلة الفقد وذلك عندما تكون الراطة على طرف المركب فقط وليست في داخل المركب .







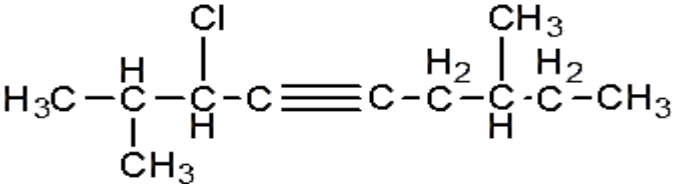
Internal alkynes (Non-Terminal Alkyne) have no exceptionally acidic hydrogens.

Relative Acidity of the Hydrocarbon.

Terminal alkynes, are more acidic than other hydrocarbons

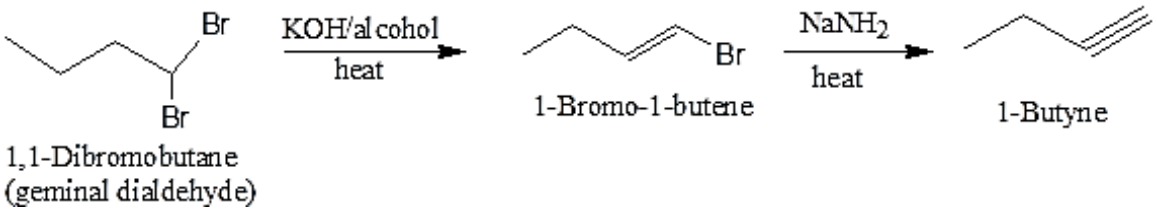
Preparation of Alkynes

Dehydrohalogenation of Alkyl dihalides

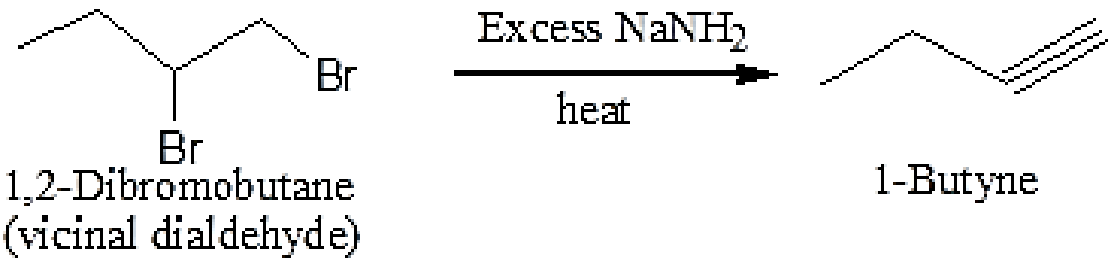


يحضر عن طريق نزع Hxمن الالكيل ثنائي الهاليد عن طريق نزع 2HX

الاولى عن طريق KOH/alchol والتسخين والثانية عن طريق NaNH2 وحرارة

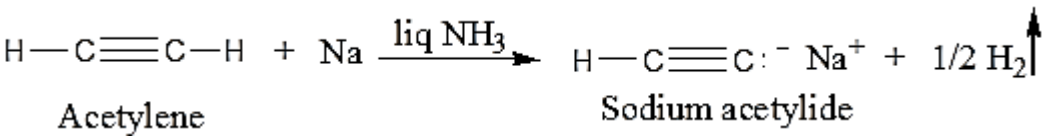


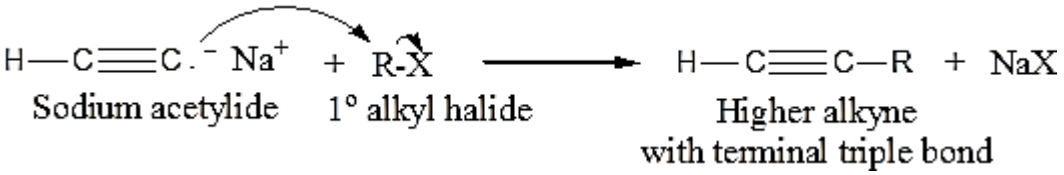
او عن طريق زيادة من NaNH2 والتسخين ينزع ايضا 2HX مرة واحدة

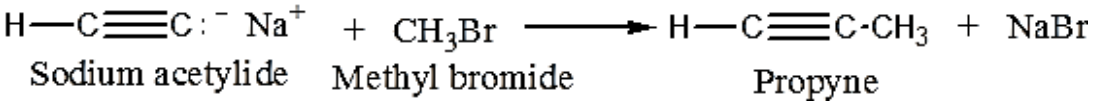


Reaction of Sodium Acetylide with Primary Alkyl Halides

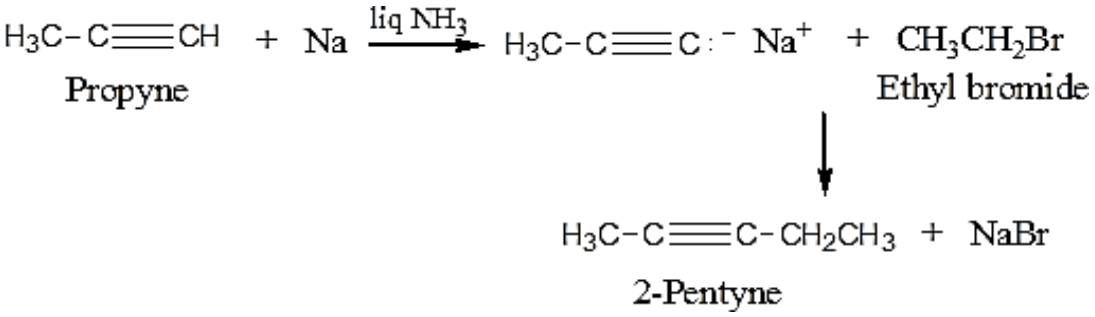
Acetylene







Monosubstituted Acetylenes

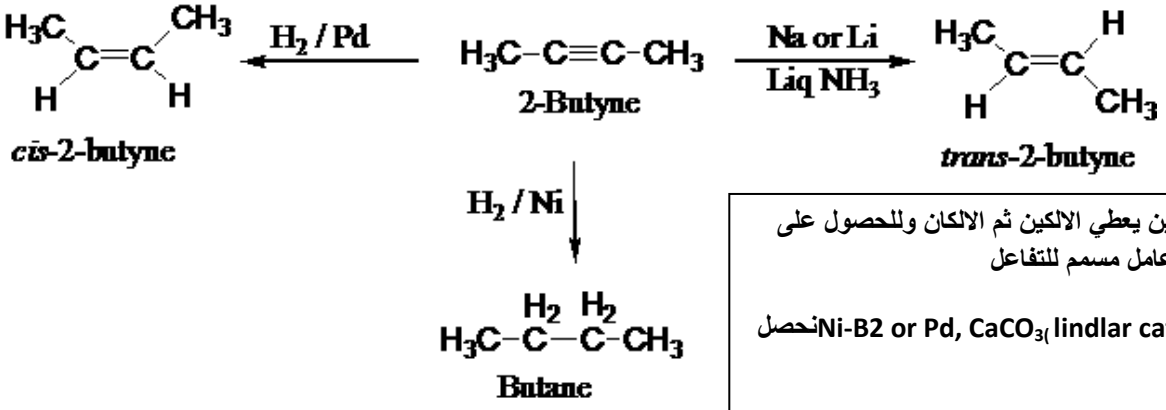


Electrophilic Addition Reactions

Addition of Hydrogen: Hydrogenation

With an ordinary nickel or platinum catalyst, alkynes are hydrogenated all the way to alkanes.

However, a special palladium catalyst (called Lindlar's catalyst) can control hydrogen addition so that only one mole of hydrogen adds. In this case, the product is a *cis* alkene.



عند إضافة الهيدروجين يعطي الالكين ثم الالكان وللحصول على الالكين فقط نستخدم عامل مسمم للتفاعل

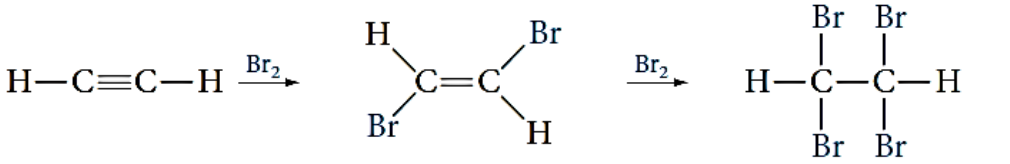
اذا استخدمنا (lindlar catalyst) Ni-B2 or Pd, $CaCO_3$ نحصل على cis alkene

ما عند استخدام Na or LI in liquid ammonia

نحصل على trans alkene

Addition of Halogen: Halogenation

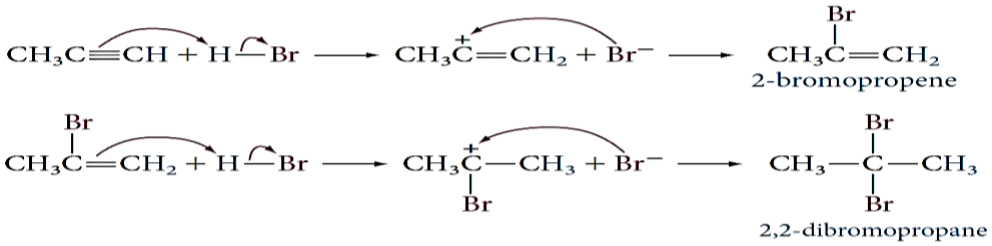
Bromine adds as follows; In the first step, the addition occurs mainly *trans.*



ethyne — *trans*-1,2-dibromoethene — 1,1,2,2-tetrabromoethane

Addition of Hydrogen Halide

With unsymmetric triple bonds and unsymmetric reagents, Markovnikov's Rule is followed in each step, as shown in the following example:



Addition of Water: Hydration

Addition of water to alkynes requires not only an acid catalyst but mercuric ion as well.

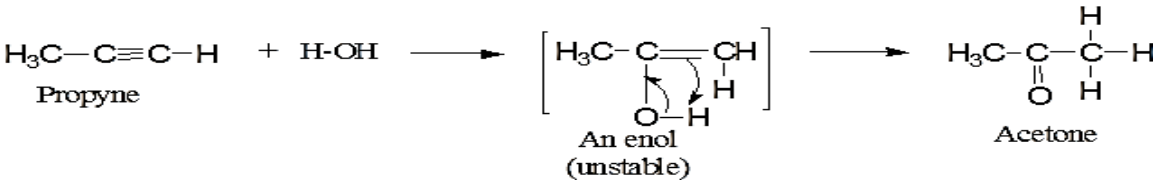
Although the reaction is similar to that of alkenes, the initial product - a vinyl alcohol or enol - rearranges to a carbonyl compound (keto form).

The keto form of aldehydes and ketones are in equilibrium with the enol form.

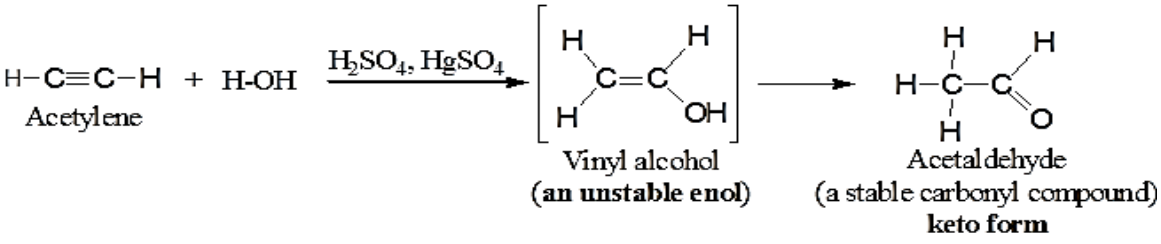
.The keto from predominates at equilibrium for most simple aldehydes and ketones

The inter conversion is called keto-enol tautomerization.

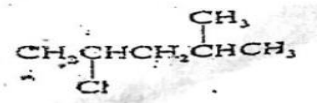
عند إضافة الماءعلى الالكاين في حالة الاستلين فقط يعطي الدهيد



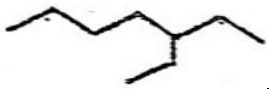
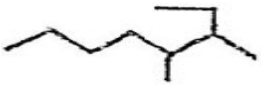
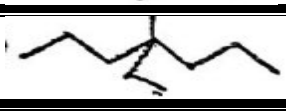
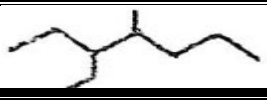
لكن اي الكاين اخر يعطي كيتون

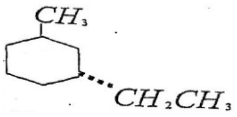


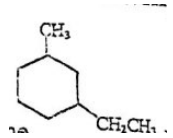
مهمة جدا

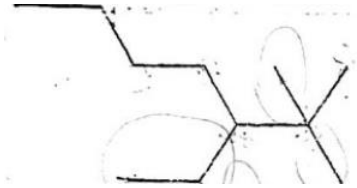
1	**What is the correct IUPAC name of the following compoung?** 		
A	**2- methyl -4-chloropentane**	**b**	**4-chloro-2-methylpenatne**
c	**2-chloro-4-methylpentane**	**d**	**2-chloro-2-methylpentane**

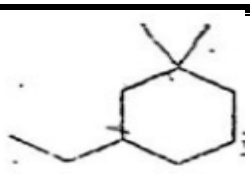
2	**Cis -1,2-dimethylcyclopentane compound is :**		
A		**b**	
c		**d**	

3	The structural formula of 3- ethyl -4- methylheptane is:		
A		b	
c		d	

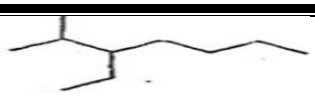
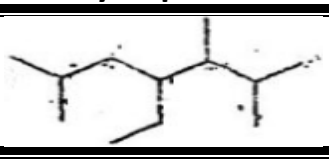
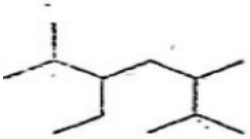
4	IUPAC name for the following compound is 		
A	Trans-1-methyl-3-ethylcyclohexene	b	cis-1-methyl-3-ethylcyclohexene
c	Trans-1-ethyl-3-methylcyclohexane	d	Trans-1-ethyl-5-methylcyclohexane

5	IUPAC name for the following compound is 		
A	1-ethyl-3-methylcyclohexane	b	1-ethyl-5-methylcyclohexane
c	3-methyl-1-ethylcyclohexane	d	1-ethyl-3-methylhexane

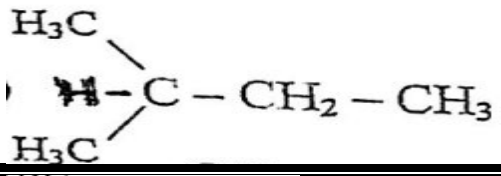
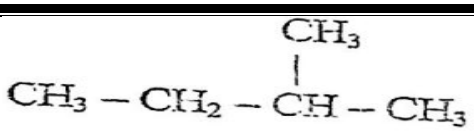
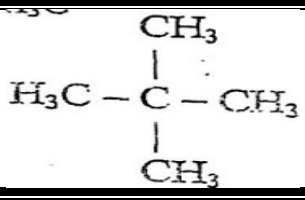
6	the IUPAC name of the formula is: 		
A	5-ethyl-6,6-dimethylheptane	b	3-ethyl-2,2-dimethylheptane
c	2,2-dimethyl-3- ethylheptane	d	6,6 di methyl-5- ethyl heptane

7	the IUPAC name of the formula is 

A	1-ethyl-3,3-dimethylcyclohexane	b	1,1dimethyl-3-ethylcyclohexane
c	3-ethyl-1,1dimethylcyclohexane	d	1-ethyl-5,5-dimethylcyclohexane

8	The structural formula of 4-ethyl -2,3,6-trimethylheptane		
A		b	
c		d	

9	The compound with the lowest boiling point is ?		
A	N-Hexane	b	2-methylpentane
c	3-methylpentane	d	2,2-dimethylbutane

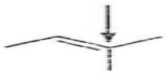
10	The molecule with the lowest boiling point is?		
A	$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$	b	
c		d	

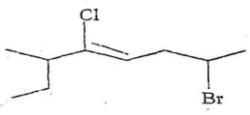
11	The compound with the highest boiling point is:		
A	N-Hexane	b	n-pentane
c	2-methylpentane	d	2,2dimethylbutane

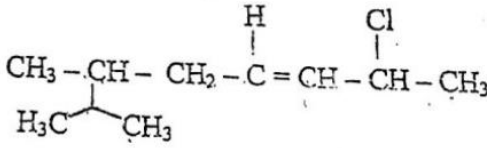
12	The product of the following reaction is: $(CH_3CH_2CH_2)_2CuLi \xrightarrow{CH_3CH_2Br}$		
A	1-bromopentane	b	1-bromopropane
c	Pentane	d	Octane

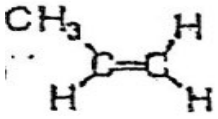
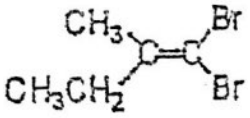
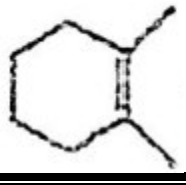
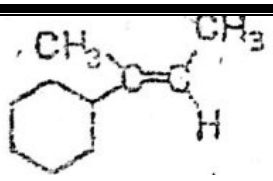
13	The product of the following reaction $(C_2H_5)_2CuLi \xrightarrow{C_2H_5Cl}$ is:		
A	1-chloroethane	b	Hexane
c	1-chlorobutane	d	Butane

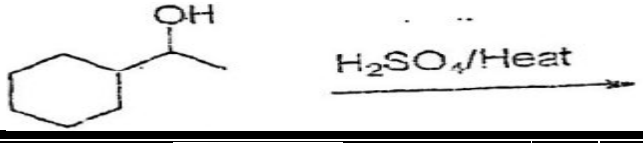
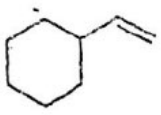
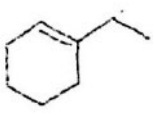
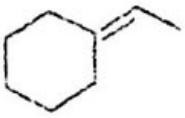
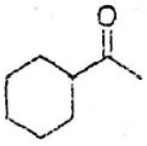
14	the reagent needed for the following transformation 		
A	Cl_2/light	b	$Cl_2/FeCl_3$
c	HCl	d	HCl/H_2O

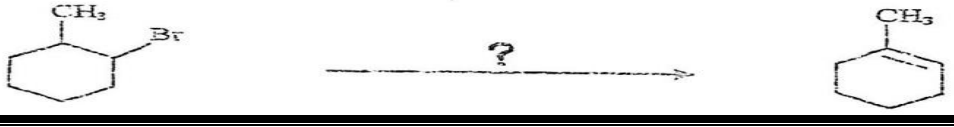
15	The type of hybridization of indicated carbo in the following structure is: 		
A	SP	b	SP^3
c	SP^3D	d	SP^2

16	The correct name of the following compound : 		
A	2-bromo-5-chloro-2-ethyl-4-octene	b	7-bromo-4-chloro-3-methyl-4-octene
c	2-bromo-5-chloro-6-methyl-4-octene	d	6-bromo-3-chloro-2-ethyl-4-heptene

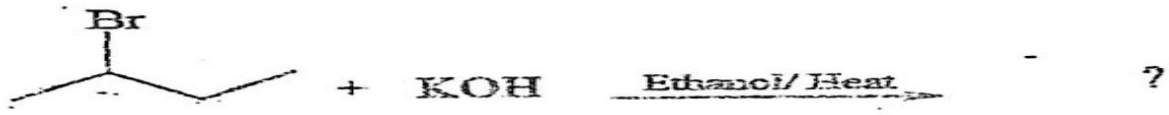
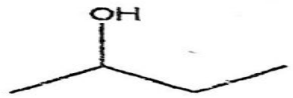
17	The correct name of the following compound 		
A	7-chloro-2,3-diethyl-5-octene	b	2-chloro-6-isopropyl-3-heptene
c	6-chloro-2-isopropyl-4-heptene	d	2-chloro-6,7-dimethyl-3-octene

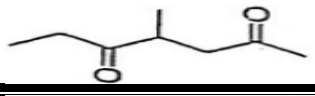
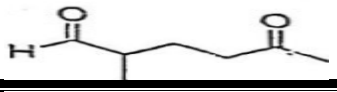
18	Which of the following compounds has two geometric isomers ?		
A		b	
c		d	

19	The major product of the following reaction is : 		
A		b	
c		d	

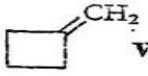
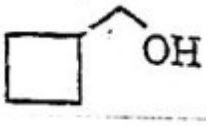
20	What the reagent used for the following reaction ? 

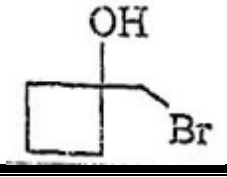
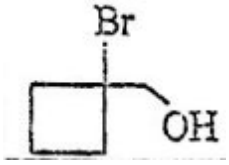
A	Conc H_2SO_4	b	KOH/Alcohol/Heat
c	Zn/acetic acid	d	Br_2, H_2O

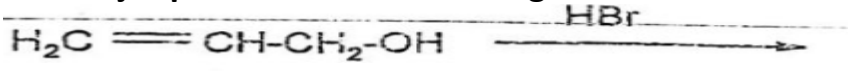
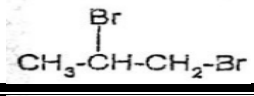
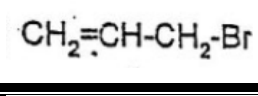
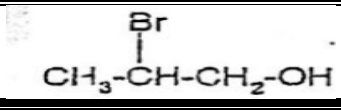
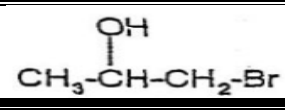
21	**The major product of the following reaction is :** 		
A		b	
c		d	

22	**Ozonoloysis of 1,3-di methylcyclopentene :**		
A		b	
c		d	

23	**Which of the following reagents is a nuclophile ?**		
A	**BF_3**	b	**NO_2^+**
c	**R-NH_2**	d	**CH_3^+**

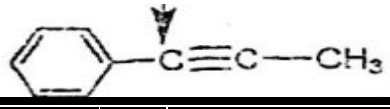
24	**The reaction of**  **with HOBr solution gives:**		
A		b	

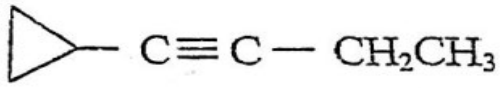
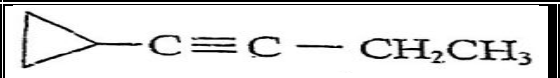
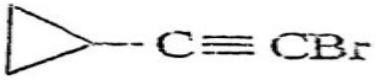
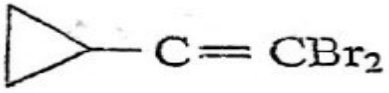
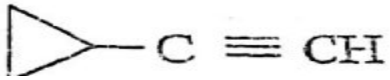
c		d	

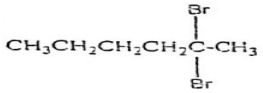
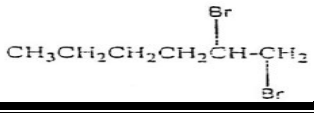
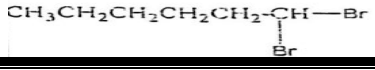
25	The major product of the following reaction is : 		
A		b	
c		d	

26	The IUPAC name of the given compound is ? 		
A	1-bromo-4-pentyne	b	5-bromo-2- pentyne
c	1-bromo-3-pentyne	d	5-bromo-3- pentyne

27	The IUPAC name of the given compound is ? 		
A	1-heptene-6-yne	b	6-heptene-1-yne
c	6-heptene-6-ene	d	1-heptene-6-ene

28	The type of hybridization of indicated carbo in the following structure is 		
A	SP	b	SP2
c	SP3	d	SP3 d

29	The unknown compound X is: X $\xrightarrow[2.CH_3\ CH_2Br]{1.NaNH_2}$ 		
A		b	
c		d	

30	The product of the following reaction is: $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C\equiv CH \xrightarrow{2\ HBr}$????????		
A		b	
c		d	$CH_3CH_2CH_2CH_2CH_2\text{-}CH_3$

Key answer

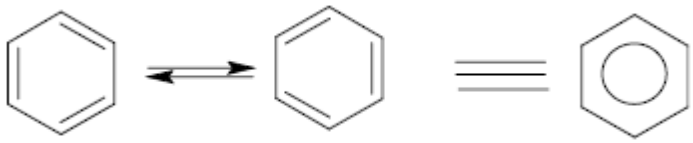
السؤال	الاجابة	السؤال	الاجابة	السؤال	الاجابة
1	c	11	a	21	d
2	b	12	c	22	b
3	d	13	d	23	c
4	c	14	a	24	c
5	a	15	d	25	c
6	b	16	c	26	b
7	c	17	d	27	a
8	b	18	d	28	a
9	d	19	c	29	d
10	d	20	b	30	a

CHAPTER 3. AROMATIC HYDROCARBONS

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

يطلق لفظ ارماتي على المركبات العضوية الحلقية غير المشبعة ويعني عطري اي ذات روائح عطرية وهناك مواد ليست بذات رائحة ولذلك سوف نستخدم المصطلح اروماتي لوصف هذة المواد

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



Their properties differ markedly from those of aliphatic hydrocarbons.

Aromatic hydrocarbons undergo electrophilic substitution whereas aliphatic hydrocarbons undergo ionic addition to double and triple bonds and free radical substitution.

The Structure of Benzene Ring

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

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

Structure of Benzene

Molecular formula = C_6H_6

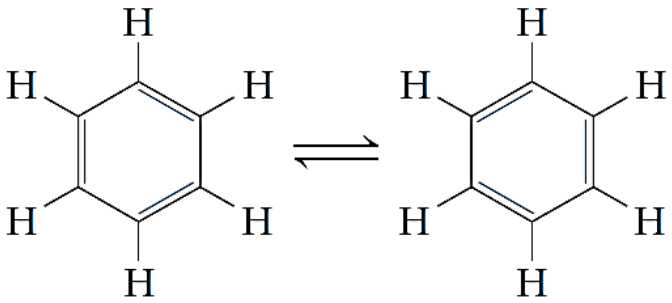
The carbon-to-hydrogen ratio in benzene, suggests a highly unsaturated structure.

Benzene reacts mainly by substitution.

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

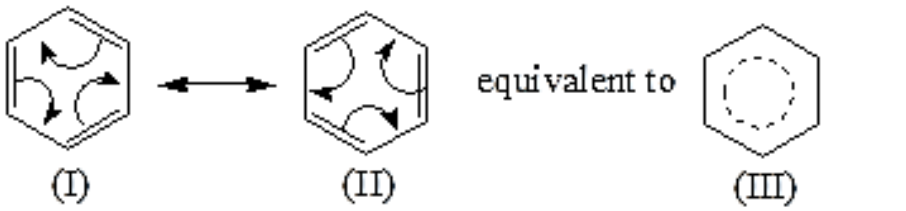
Kekulé structure for benzene.

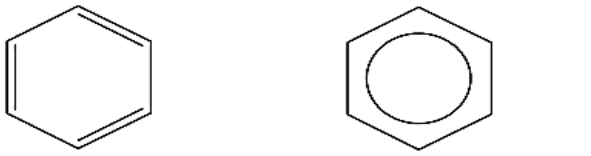
Kekulé suggested that the single and double bonds exchange positions around the ring so rapidly that the typical reactions of alkenes cannot take place.



the Kekulé structures for benzene

Resonance Model for Benzene.





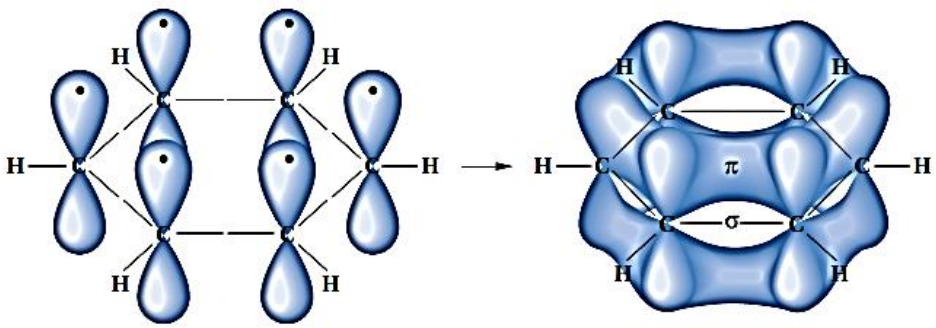
Kekulé delocalized pi cloud

Benzene is planar.

All of the carbon–carbon bond lengths are identical*: 1.39 Aº, intermediate between typical carbon–carbon bond lengths.** ***single (1.54Aº) **and** ***double (1.34 Aº)***

Each carbon is therefore *sp*2-hybridized.

Bond angles of 120°.



Aromatic Character (Aromaticity)

شروط المركب الاروماتي

لابد ان يكون المركب حلقي وتكون ذرات الكربون في مستوى واحد حتى يمكن تداخل مدارت باي بشكل يسمح بالطنين المستمر

لابد ان لا تحتوي الحلقة على ذرة كربون مفصولة اي SP3

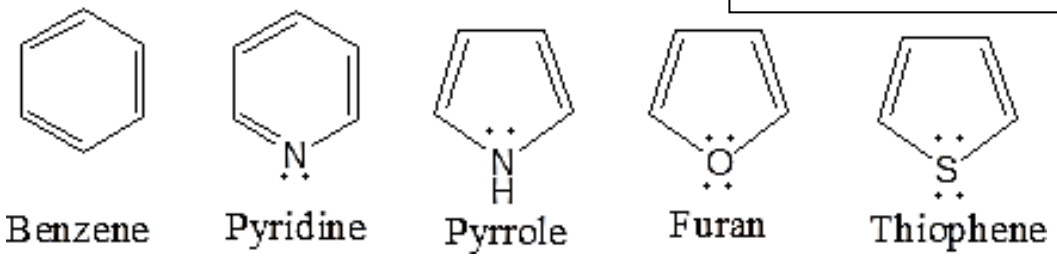
لابد ان تحقق قانون Huckel rule

Huckel rule

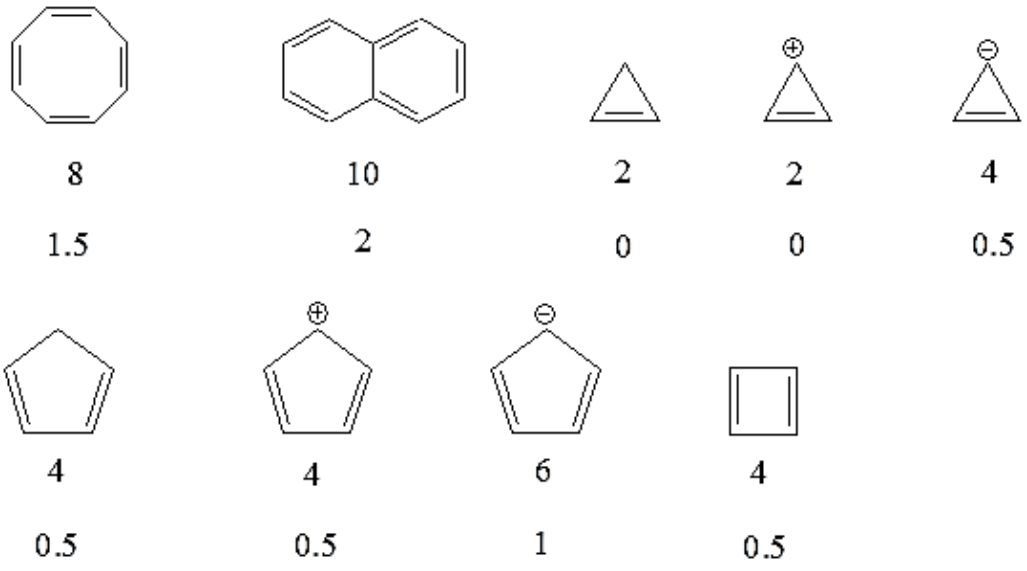
The number of ∏ electrons in the compound = (4n + 2)

Where *(n* = 0,1, 2, 3, and so on).

Structure and name of aromatic compound

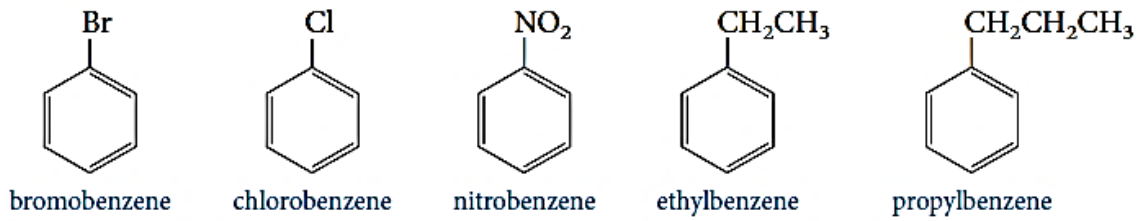


Examples

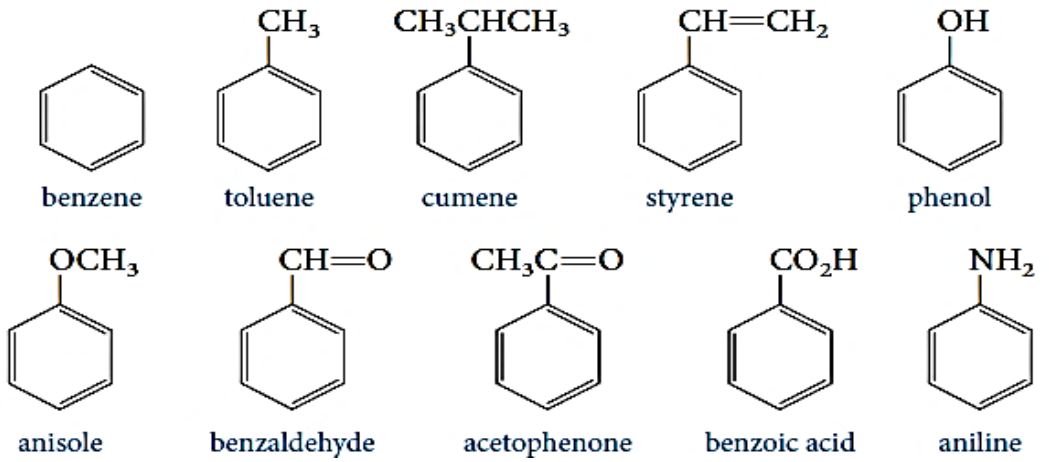


Nomenclature of Aromatic Compounds

<u>Monosubstituted benzenes</u> that do not have common names accepted by IUPAC are named as derivatives of benzene.



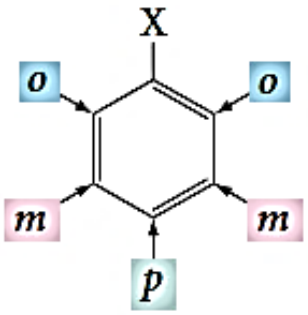
Common names are accepted by IUPAC (parent compounds).



When two substituents are present, *three isomeric structures are possible*.

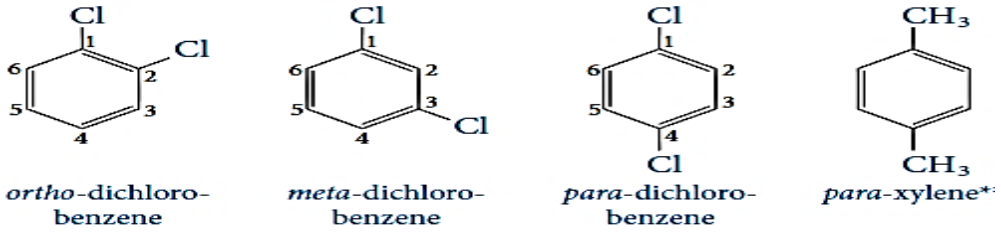
They are designated by the prefixes; *ortho*- (*o*-), *meta*- (*m*-) and *para*- (*p*-).

If substituent X is attached to carbon 1; *o*- groups are on carbons 2 and 6, *m*- groups are on carbons 3 and 5, and *p*- groups are on carbon 4.

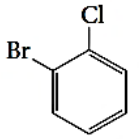


نستخدم المقطع اورثو وميتا وبارا عند وجود ذرتين هالوجين على الحلقة بحيث تأخذ احدهم رقم 1 وتأخذ الاخري الاسماء اورثو وميتا وبارا كما بالشكل

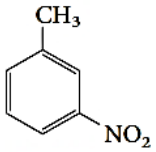
Examples;



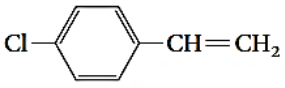
The prefixes; *ortho-* (*o-*), *meta-* (*m-*) and *para-* (*p-*) are used when the two substituents are not identical.



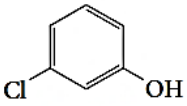
o-bromochlorobenzene
(note alphabetical order)



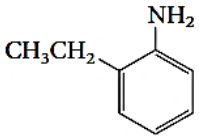
m-nitrotoluene



p-chlorostyrene

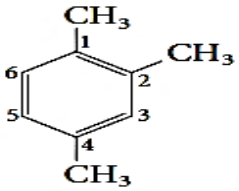


m-chlorophenol



o-ethylaniline

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



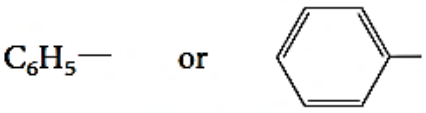
1,2,4-tri-
methylbenzene

3,5-dichlorotoluene

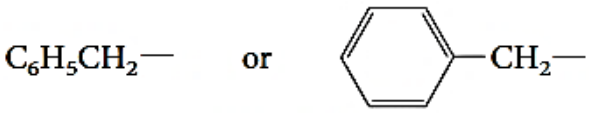
2,4,6-trinitrotoluene
(TNT)

في حالة وجود اكثر من استبدالين على الحلقة نرقم الحلقة

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



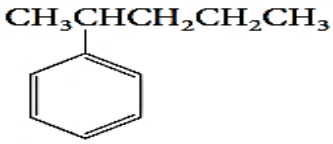
phenyl group



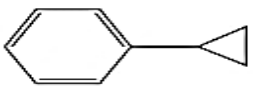
benzyl group

Examples;

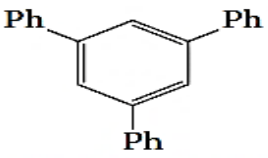
اذا وجدت حلقة البنزين ضمن سلسلة تعامل حلقة البنزين كمجموعة بديلة تأخذ الاسم فينيل (phenyl)



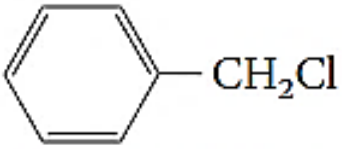
2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



1,3,5-triphenylbenzene



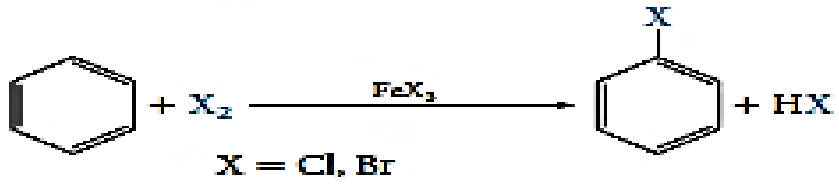
benzyl chloride

Reactions of Benzene

Electrophilic Aromatic Substitution Reactions

تفاعلات الاستبدال الالكتروفيلي

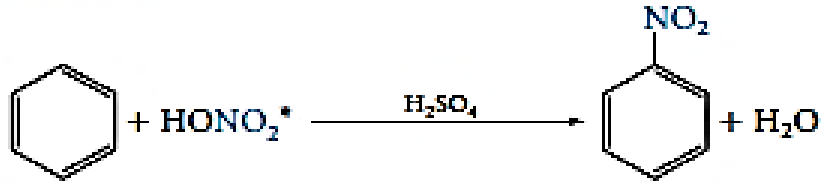
Halogenation



تفاعلات الهلجنة تتم بواسطة هالوجين واحد أحماض لويس المناسبة كعامل حفاز

تخرج Hتدخل X

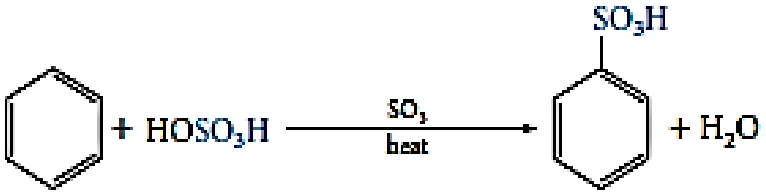
Nitration



تفاعلات النيترة تتم بواسطة HNO_3 فر وجود H_2SO_4 كعامل مساعد

تخرج Hتدخل مجموعة NO2

Sulfonation

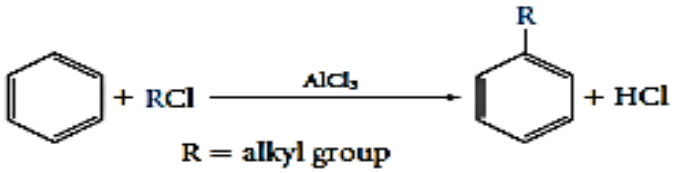


تفاعلات السلفنة بواسطةH_2SO_4

في وجود SO_3كعامل مساعد

تخرج Hتدخل SO_3H

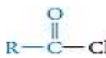
Alkylation (Friedel-Crafts)



الكلة (فريدل كرافت) بواسطة هاليد الالكيل في وجود $Al\ Cl_3$لا مائي

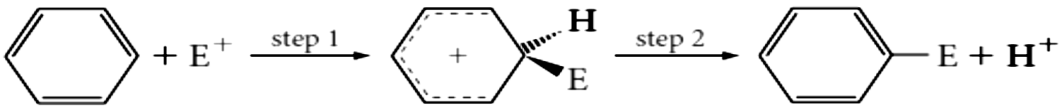
تخرج ال Hتدخل R

Acylation (Friedel-Crafts)

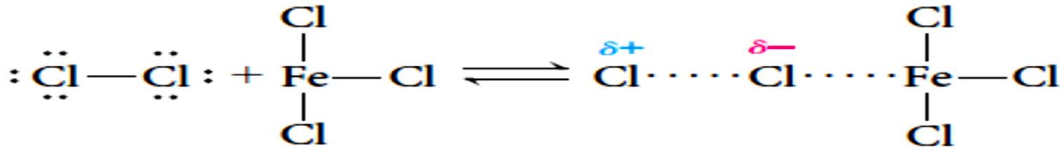
اسيلة (فرديل كرافت) بواسطة 
في وجود $Al\ Cl_3$لا مائي تخرج Hوتدخل

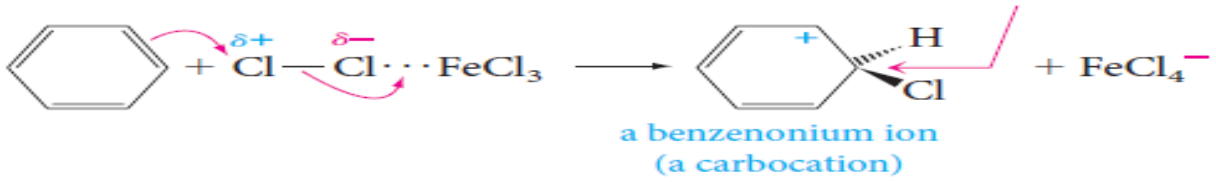
The Mechanism of Electrophilic Aromatic Substitution

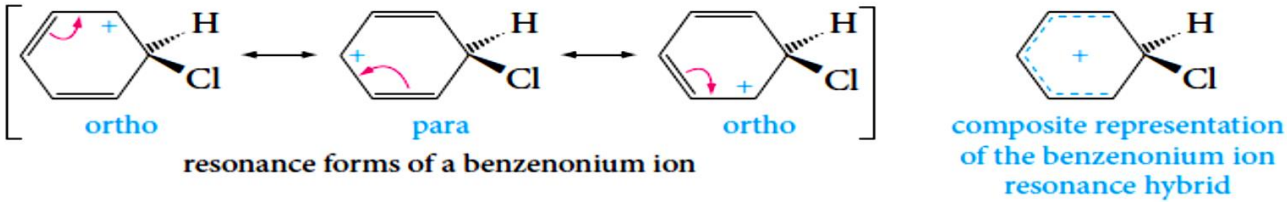
We can generalize this two-step mechanism for all the electrophilic aromatic substitutions.



Halogenation



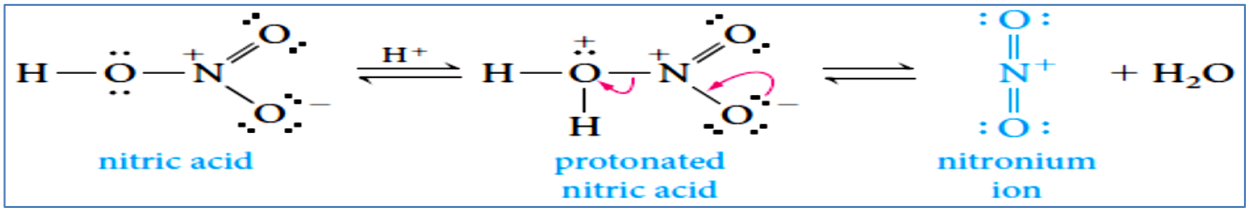




The Mechanism of Electrophilic Aromatic Substitution

Nitration

In aromatic nitration reactions, the sulfuric acid catalyst protonates the nitric acid, which then loses water to generate the nitronium ion (NO_2^+), which contains a positively charged nitrogen atom.

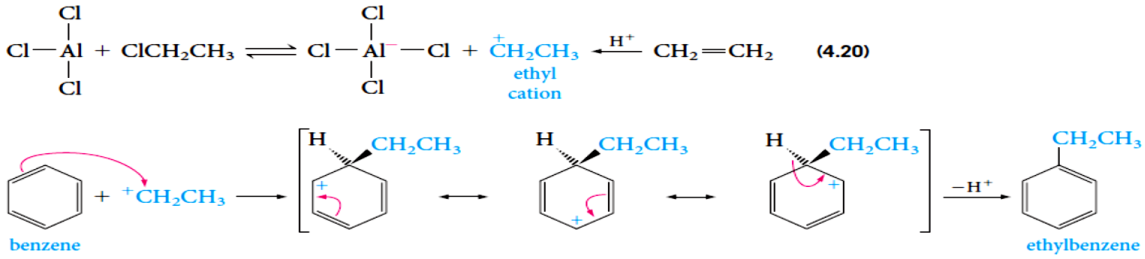


Sulfonation

We use either concentrated or fuming sulfuric acid, and the electrophile may be sulfur trioxide, SO_3, or protonated sulfur trioxide, $^+SO_3H$.

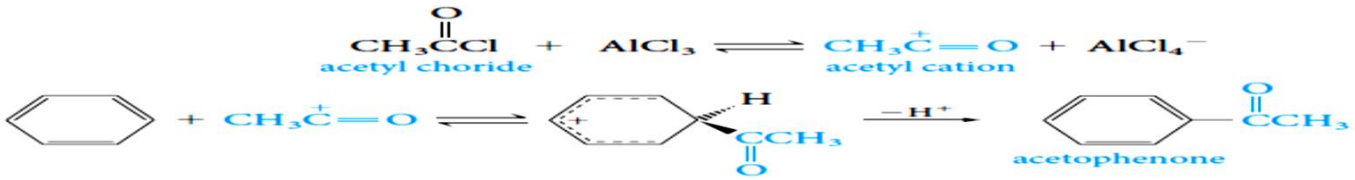
Friedel–Crafts Alkylation

The electrophile is a carbocation, which can be formed either by removing a halide ion from an alkyl halide with a Lewis acid catalyst (for example, $AlCl_3$) .



Friedel–Crafts Acylation

The electrophile is an acyl cation generated from an acid derivative, usually an acyl halide. The reaction provides a useful general route to aromatic ketones.



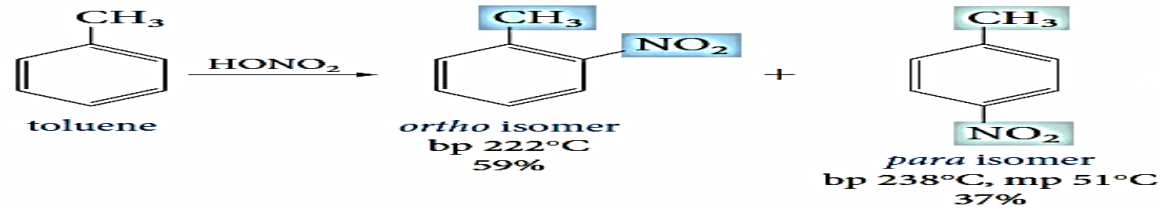
Disubstituted Benzenes:

Orientation

المجموعة	مشبعة او هالوجين	غير مشبعة
التوجية للاستبدال الثاني على الحلقة	Ortho and para	meta
تنشيط الحلقة	المجموعات المشبعة تعطي الكترونات للحلقة و تسوي activating لكن الهالوجينات هي مجموعات مثبطة للحلقة وتقلل النشاط deactivating	Deactivating benzene ring (تحتوي على روابط ثنائية وثلاثية)
مثل	NH2, OH , OR , C6H5 , R F ,Cl , Br , I	NO2 , CN , COOH , CHO , SO3H , CO2R , COR

Substituents already present on an aromatic ring determine the position taken by a new substituent.

Example; nitration of toluene gives mainly a mixture of *o*- and *p*-nitrotoluene.



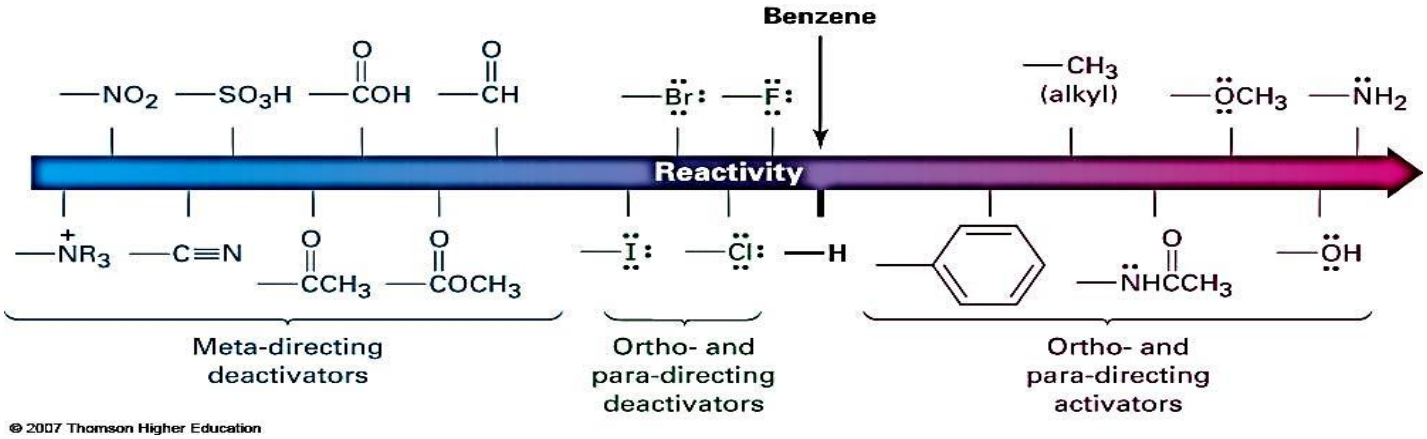
On the other hand, nitration of nitrobenzene under similar conditions gives mainly the *meta* isomer.

Disubstituted Benzenes: Orientation& Reactivity

Directing and Activating Effects of Common Functional Groups

Substituents that release electrons to the ring will activate the ring toward electrophilic substitution.

Substituents that withdraw electrons from the ring will deactivate the ring toward electrophilic substitution.



If the directing effects of the two groups are the same, the result is additive ■

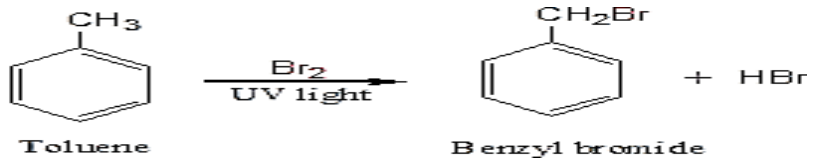
p-Nitrotoluene 2-Bromo-4-nitrotoluene

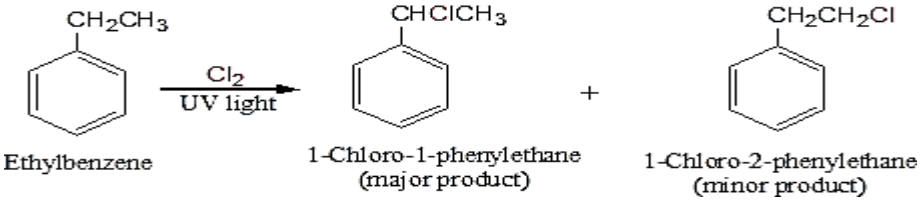
If the directing effects of two groups oppose each other, the more powerful ■ activating group decides the principal outcome

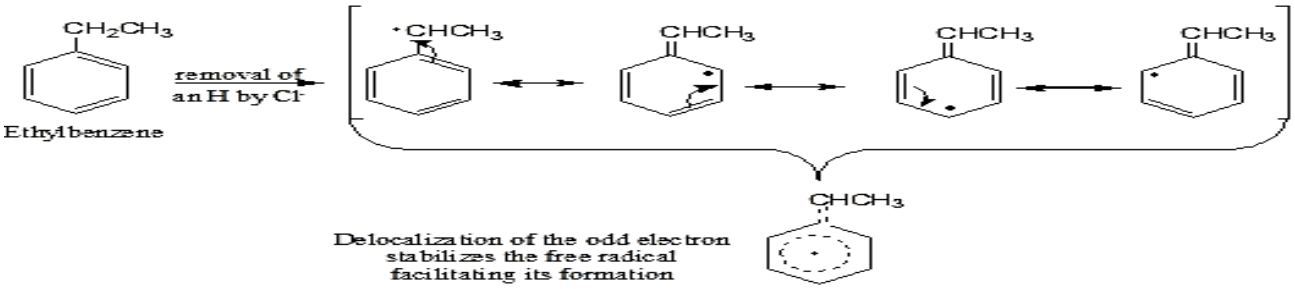
Usually gives mixtures of products ■

p-Methylphenol 4-Methyl-2-nitrophenol

Side-Chain Reactions of Benzene-Derivatives



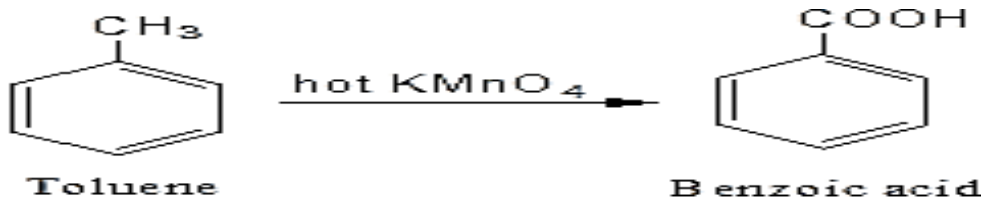


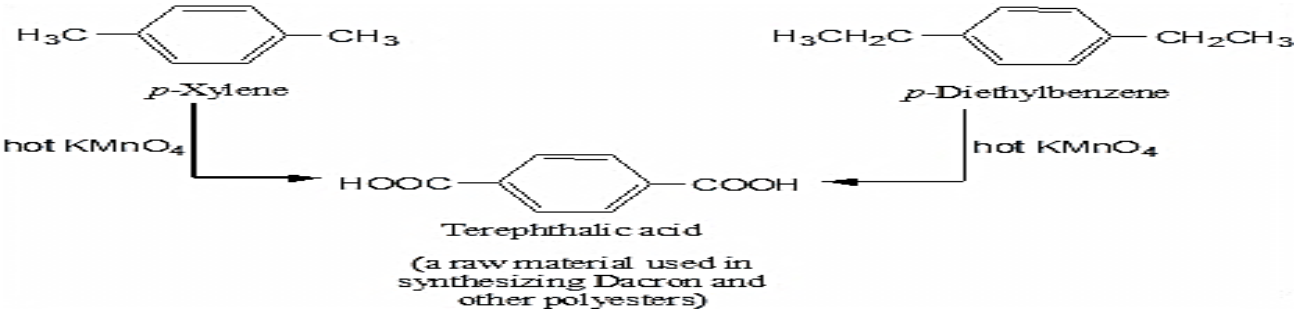


2. Oxidation of an Alkyl Side Chain

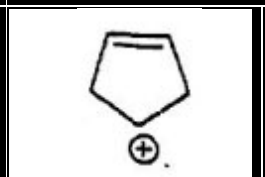
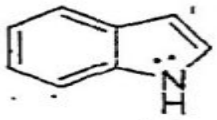
Conversion into a carboxyl group, -COOH, by treatment with hot potassium permanganate.

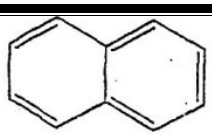
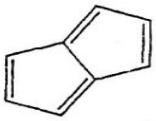
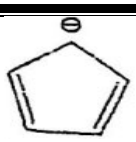
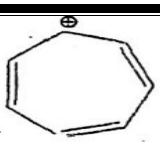
Regardless the length of the alkyl chain, the product is always the same.

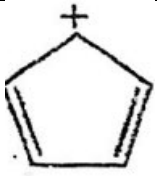
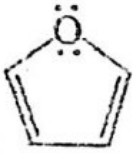
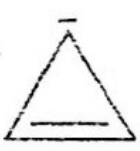


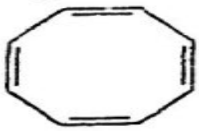
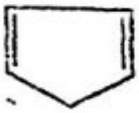
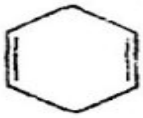
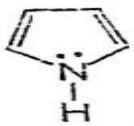


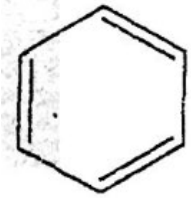
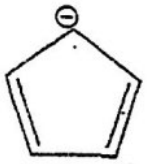
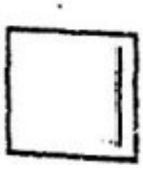
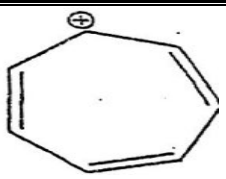
مهما كان طول السلسلة الجانبية تتحول الى حمض كربوكسيلي ما عدا T- butyl لانه لا يتأكسد

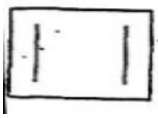
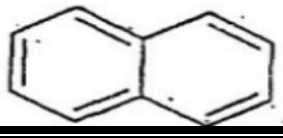
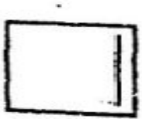
1	Which of the following compounds is aromatic ?						
A		b		c		d	

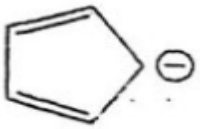
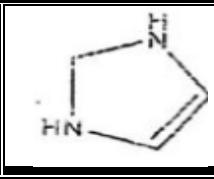
2	Which of the following compounds is not aromatic ?						
A		b		c		d	

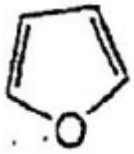
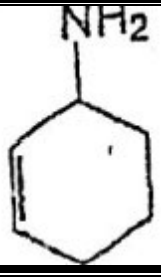
3	Which of the following compounds is aromatic ?						
A		b		c		d	

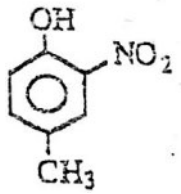
4	Which of the following compounds has an aromatic character ?							
A		b		c		d		

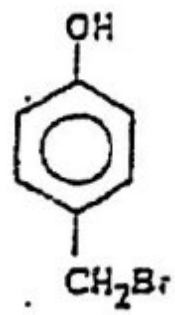
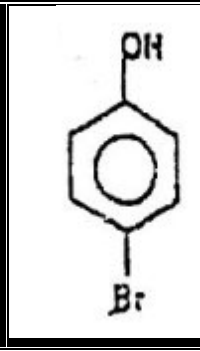
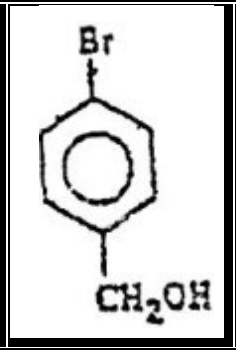
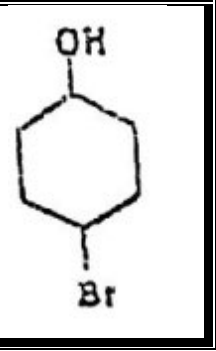
5	Which of the following compounds is not aromatic ?							
A		b		c		d		

6	Which of the following compounds is aromatic ?							
A		b		c		d		

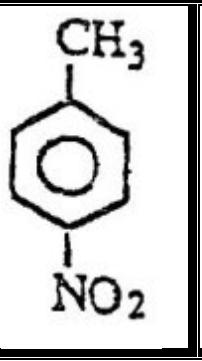
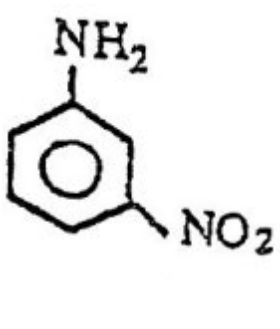
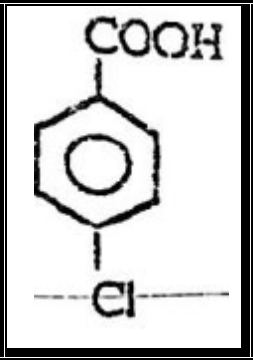
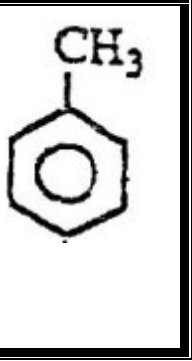
7	Which of the following compounds is aromatic ?							
A		b		c		d		

8	Which of the following compounds is aromatic ?							
A		b		c		d		

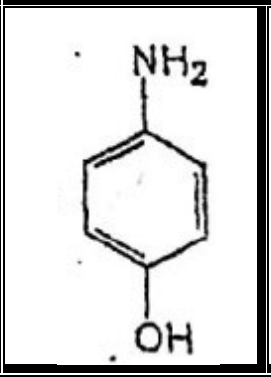
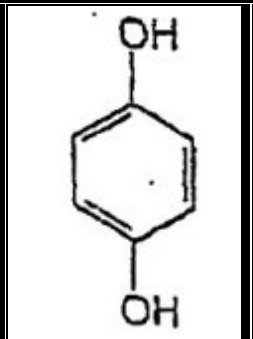
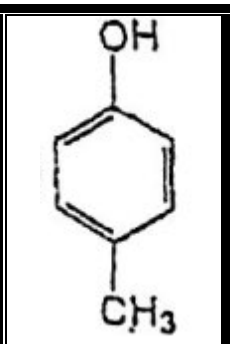
9	what the IUPAC name of this compound ? 		
A	4-Methyl-2-nitrophenol	b	2-Nitro-p-methylphenol
c	o-Nitrohydroxytoluene	d	2-Methyl-4-nitrophenol

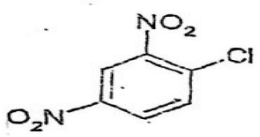
10	Which of the following compounds is 4- bromophenol?						
A		b		c		d	

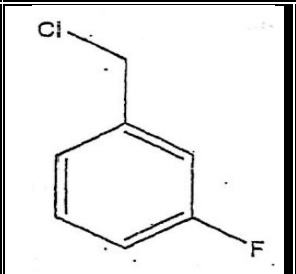
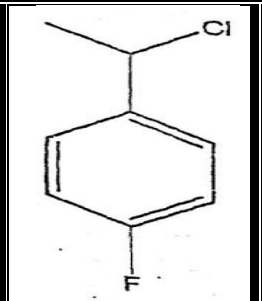
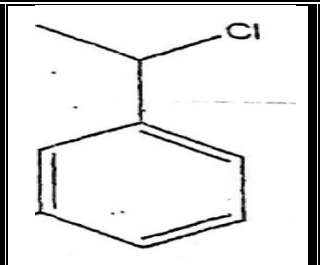
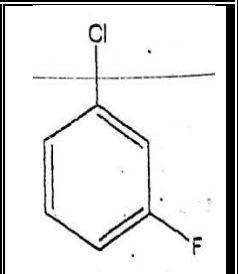
11	The common name of methylbenzene is?						
A	toluene	b	p- Cresol	c	Anisol	d	Xylene

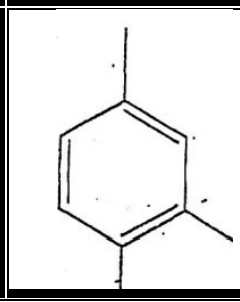
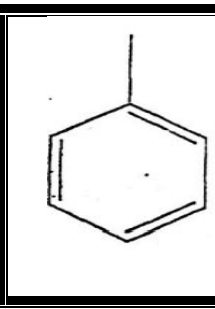
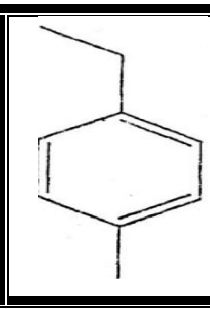
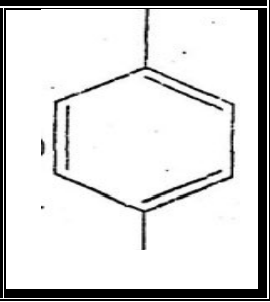
12	Which of the following compounds known as m- Nitroaniline?						
A		b		c		d	

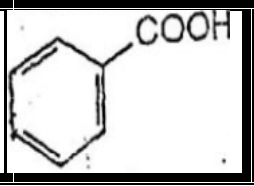
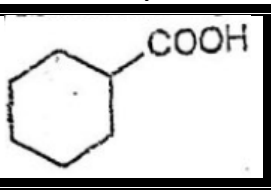
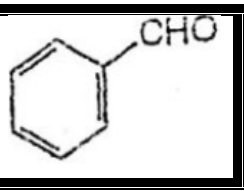
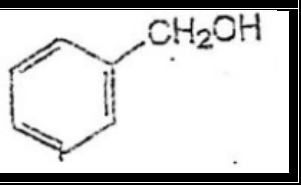
13	The common name of 1,4- dimethylbenzene?						
A	toluene	b	p- Cresol	c	p-Anisol	d	p-Xylene

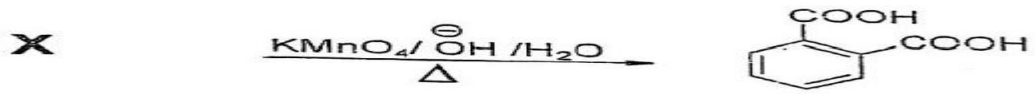
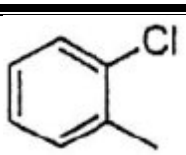
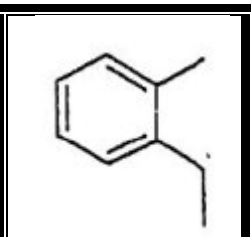
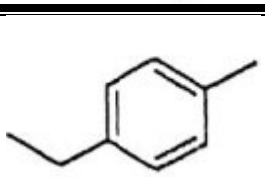
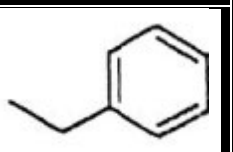
14	The structure formula of p- cresol is ?						
A		b		c		d	

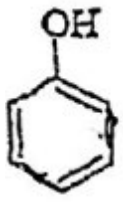
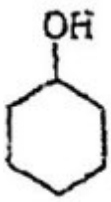
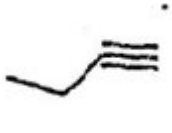
15	What the IUPAC name of the structure ? 		
A	1-chloro-2,4- diaminobenzene	b	1,3- dinitro-4-chlorobenzene
c	1-chloro-2,4- dinitrobenzene	d	1,3-diamino-4- chorobenzene

16	The structure of m-fluorobenzene chloride is?						
A		b		c		d	

17	The structure of p- xylene is ?						
A		b		c		d	

18	Oxidation of ethylbenzene by KMnO4 yields ?						
A		b		c		d	

19	The reactant X is ? 						
A		b		c		d	

20	Which of the following compounds undergoes an electrophilic substitution reaction?						
A		b		c		d	

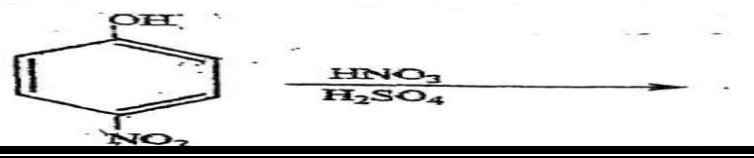
21	What is the best reagent used for the following reaction ? 						
A	Br_2, heat.	b	Br_2, CCl_4	c	Br_2, $FeBr_3$	d	CH_3Br, $AlBr_3$

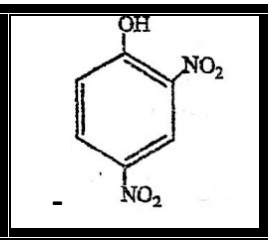
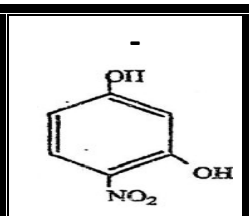
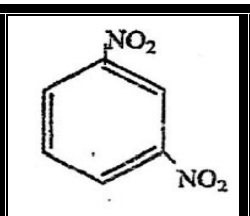
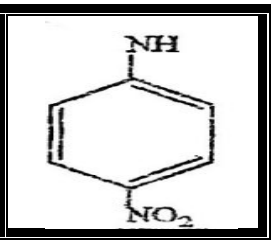
22	The carbonyl group attached with a benzene ring is:		
A	activating and meta – directing group.	b	deactivating and meta – directing group.
c	deactivating and ortho/para directing group	d	activating and ortho/para directing group

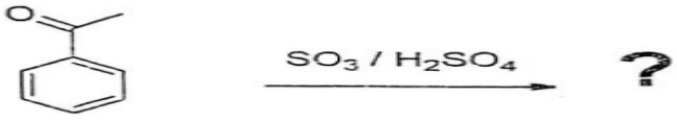
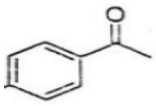
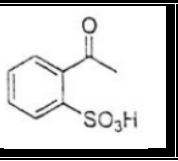
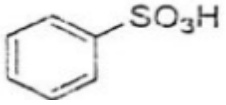
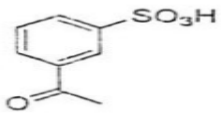
23	Which of the following groups m-directing in electrophilic substitution?						
A	$-CH_3$	b	$-NH_2$	c	$-SO_3H$	d	$-OCH_3$

24	Which of the following groups deactivated the benzene ring towards nitration?						
A	-OH	b	$-COOCH_3$	c	$-NH_2$	d	$-OCH_3$

25	Which of the following groups deactivated the benzene ring towards nitration?						
A	$-NH_2$	b	- OH	c	$-CH_3$	d	-CN

26	The main product of the reaction shown below is ? 

A		b		c		d	

27	The sulfonation prouduct formed from the following reaction is ? 						
A		b		c		d	

Key answer

السؤال	الاجابة	السؤال	الاجابة
1	D	14	C
2	B	15	C
3	C	16	D
4	D	17	D
5	D	18	A
6	B	19	B
7	B	20	A
8	C	21	C
9	A	22	B
10	B	23	C
11	A	24	B
12	B	25	D
13	D	26	A
		27	D

CHAPTER 4

ALCOHOLS, PHENOLS AND ETHERS

Alcohols, Phenols and Ethers

Alcohols, ethers and phenols have a common functional group, the hydroxyl group, -OH.

H-O-H	R-OH	R-O-R	Ph-O-H
Water	Alcohol	Ethers	Phenol

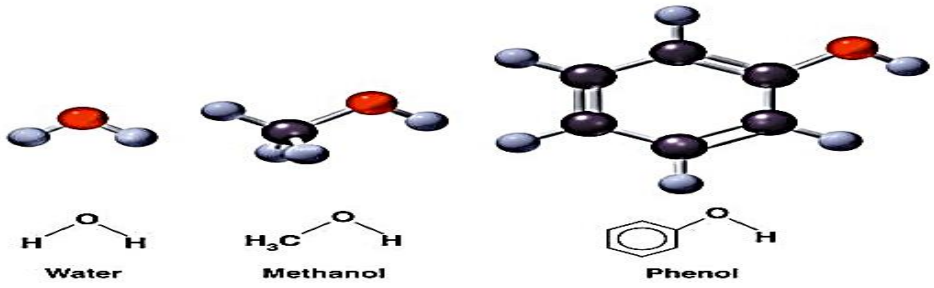
Alcohols are compounds whose molecules have a hydroxyl group attached to a *saturated* carbon atom.

Phenols are compounds that have a hydroxyl group attached directly to a ***benzene ring*** **.**

Ethers are compounds whose molecules have an oxygen atom bonded to two carbon atom.

Alcohols and Phenols

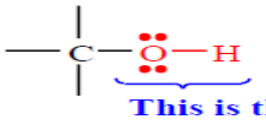
Alcohols and phenols may be viewed as organic *derivatives of water*.



Alcohols have the general formula R-OH, and structurally similar to water, but with one of the hydrogens replaced by an alkyl group.

Phenols have a hydroxyl group attached directly to an aromatic ring.

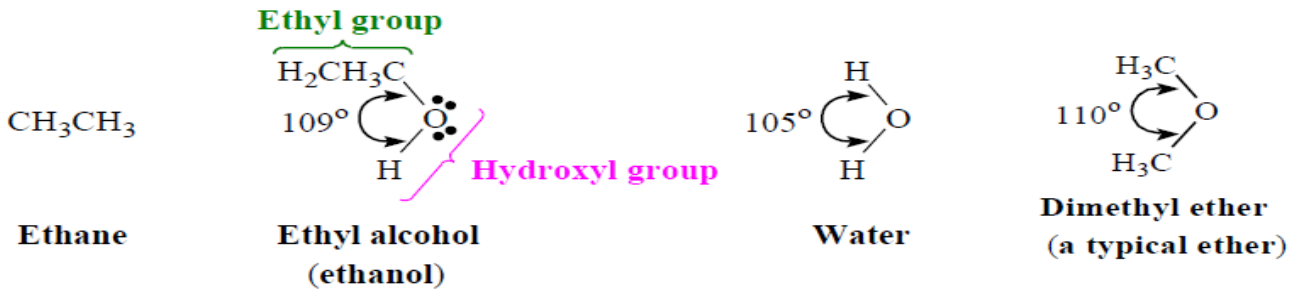
Alcohols



Alcohols can be viewed in two ways structurally:

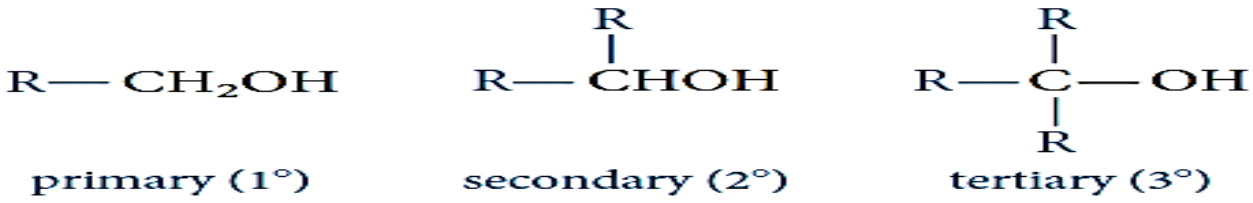
as **hydroxyl derivatives** of alkanes

and (2) as **alkyl derivatives** of water.



Classification of Alcohols

Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.



Methyl alcohol, which is not strictly covered by this classification, is usually grouped with the primary alcohols.

Nomenclature of Alcohols

The **common names** for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word alcohol: Alkyl *alcohol* .

alkyl group + alcohol **في التسمية الشائعة يتم ذكر مجموعة الالكيل يتبعها كلمة الكحول**

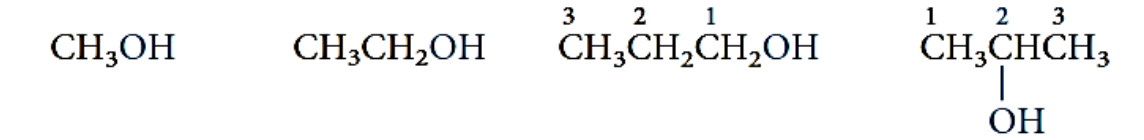
In the **IUPAC system,** alcohols are named according to the following rules.

1. Select the longest continuous carbon chain that *contains the* -OH *group.*

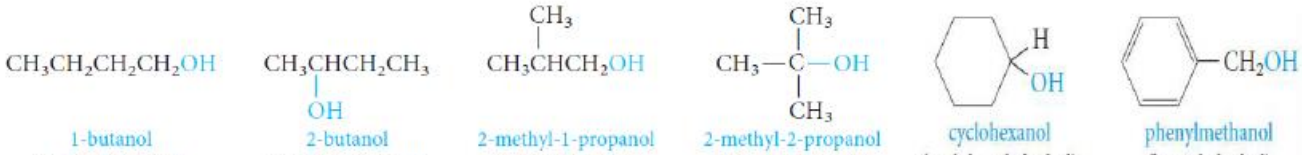
Drop the *–e* ending of the parent alkane and replace it by the suffix *-ol: Alkanol*

2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the *lowest possible number.*

نختار اول سلسلة تحتوي على مجموعة الهيدروكسيل ونستبدل الحرف e بالمقطع ol



methanol (methyl alcohol) — ethanol (ethyl alcohol) — 1-propanol (*n*-propyl alcohol) — 2-propanol (isopropyl alcohol)

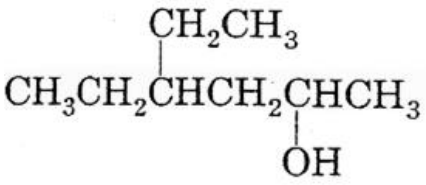


1-butanol (*n*-butyl alcohol) — 2-butanol (*sec*-butyl alcohol) — 2-methyl-1-propanol (isobutyl alcohol) — 2-methyl-2-propanol (*tert*-butyl alcohol) — cyclohexanol (cyclohexyl alcohol) — phenylmethanol (benzyl alcohol)

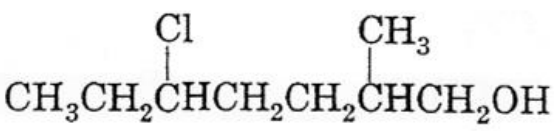
3. When alkyl side chains or other groups are present, they are named alphabetically and their positions are indicated by a number.

The position of the functional group (-OH) is always given the lowest possible number at the end of the name.

عند وجود تفرعات نرقم بحيث مجموعة ال oH تأخذ أقل رقم ممكن وفي حالة المركبات الحلقية نبدأ الترقيم من عندها ولا داعي لذكر رقمها .

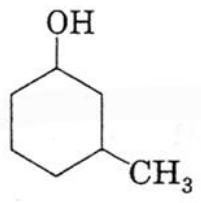


4-Ethyl-2-hexanol (*not* 3-Ethyl-5-hexanol)

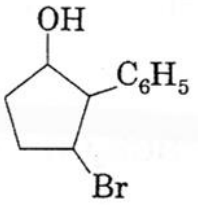


5-Chloro-2-methyl-1-heptanol (*not* 3-Chloro-6-methyl-7-heptanol)

For cyclic alcohols, numbering always starts from the carbon bearing the -OH group.



3-Methylcyclohexanol
(*not* 1-Methyl-3-cyclohexanol)

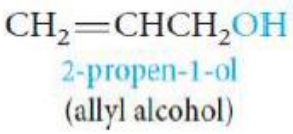


3-Bromo-2-phenylcyclopentanol
(*not* 1-Bromo-2-phenyl-3-cyclopentanol)

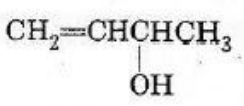
4. With Unsaturated Alcohols; If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

مجموعة ال oH لها أسبقية عن الرابطة الثنائية والثلاثية في الترقيم .

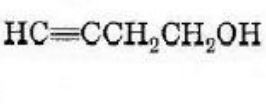
The name should include (if possible) both the hydroxyl and the unsaturated groups, even if this does not make the longest chain the parent hydrocarbon.



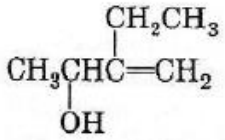
2-propen-1-ol
(allyl alcohol)



3-Buten-2-ol
(*not* 1-Buten-3-ol)



3-Butyn-1-ol
(*not* 1-Butyn-4-ol)



3-Ethyl-3-buten-2-ol
(longest chain including C=C)

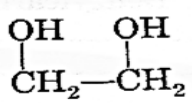
Alcohols with More Than One Hydroxyl Group

بعض الامثلة على الكحولات عديدة الكربوكسيل (وردت بالاختبارات السابقة)

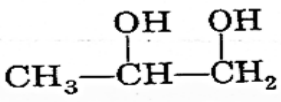
Compounds with two adjacent alcohol groups are called *glycols*.

The most important example is ethylene glycol.

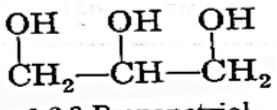
Compounds with more than two hydroxyl groups are also known, and several, such as glycerol and sorbitol, are important commercial chemicals.



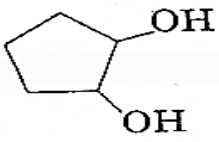
IUPAC name: 1,2-Ethanediol
Common name: Ethylene glycol



1,2-Propanediol
Propylene glycol



1,2,3-Propanetriol
Glycerol or Glycerin



IUPAC name: 1,2-Cyclopentanediol

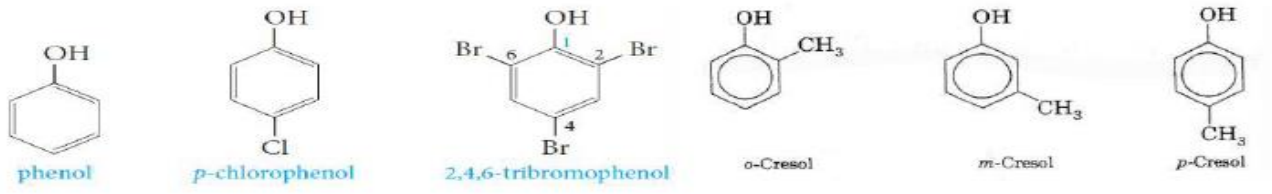
<u>Ethylene glycol</u> is used as the "permanent" antifreeze in automobile radiators and as a raw material in the manufacture of Dacron.

<u>Ethylene</u> glycol is completely miscible with water.

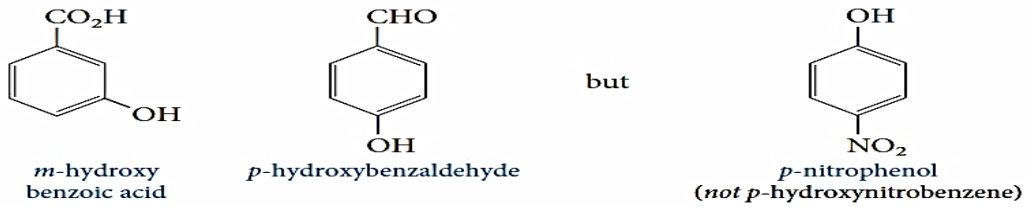
<u>Glycerol</u> is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing qualities make it useful in shaving and toilet soaps and in cough drops and syrups.

Phenols

are usually named as derivatives of the parent compounds.



The hydroxyl group is named as a substituent when it occurs in the same molecule with carboxylic acid, aldehyde, or ketone functionalities, which have **priority in naming.**



Physical Properties of Alcohols

Physical State

The simplest alcohol, methanol, is a liquid at room temperature.

In contrast, alkanes from methane to butane are gases.

Solubility

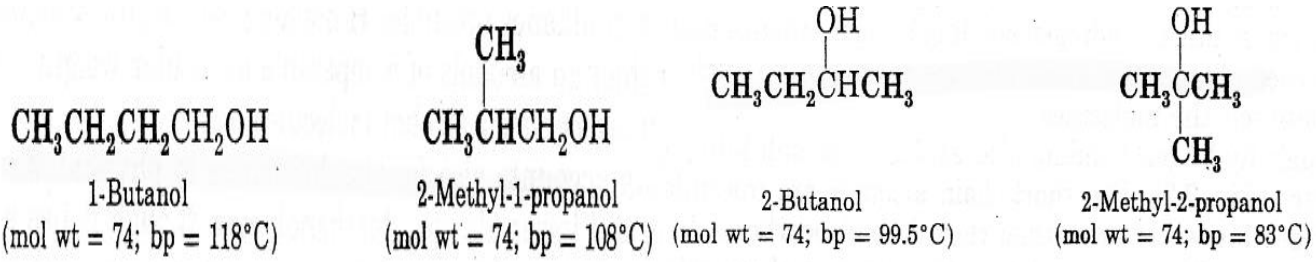
The lower alcohols are completely miscible with water.

As the number of carbons in the alcohol increases, the solubility in water decreases.

Boiling Points

Series of normal alcohols; The boiling points increase with increase in molecular weights.

A comparison of boiling points among isomeric alcohols; The boiling points decrease as the number of alkyl branches from the carbinol group increases.



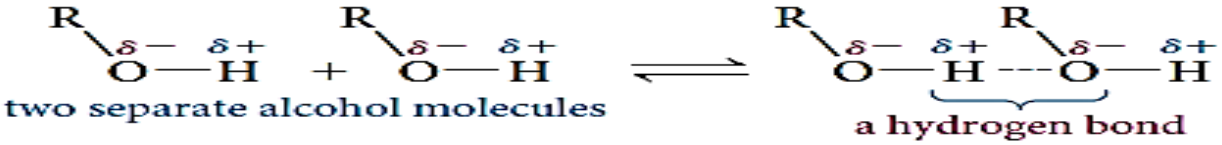
Hydrogen Bonding in Alcohols

The **boiling points** (bp's) of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
mol wt	46	46	44
bp	+78.5°C	−24°C	−42°C

Why? **Because alcohols form hydrogen bonds with one another.**

The O-H bond is polarized by the high electronegativity of the oxygen atom and places a partial positive charge on the hydrogen atom and a partial negative charge on the oxygen atom.



However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon like, its water solubility decreases.

كلما زادت طول السلسلة الكربونية زادت درجة الغليان

Table 7.1 Boiling Point and Water Solubility of Some Alcohols

Name	Formula	bp, °C	Solubility in H_2O g/100 g at 20°C
methanol	CH_3OH	65	completely miscible
ethanol	CH_3CH_2OH	78.5	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	97	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

ترتيب درجة الغليان 1^0 alc > 2^0 alc > 3^0 alc

Physical Properties of Phenols

Phenol is a colorless, crystalline, low-melting solid, with a high boiling point, that is moderately soluble in water.

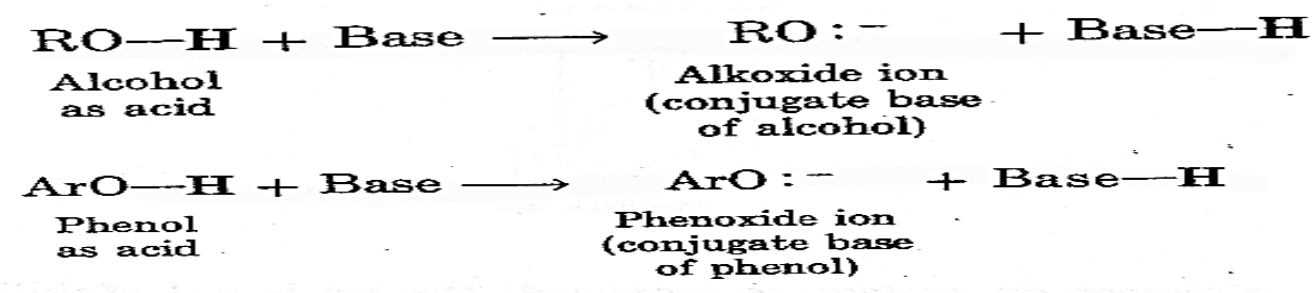
Most other phenols also are solids, with slight solubility in water and high boiling points.

The most significant physical property that distinguishes alcohols from phenols is the **acidity of phenols.**

The Acidity of Alcohols and Phenols

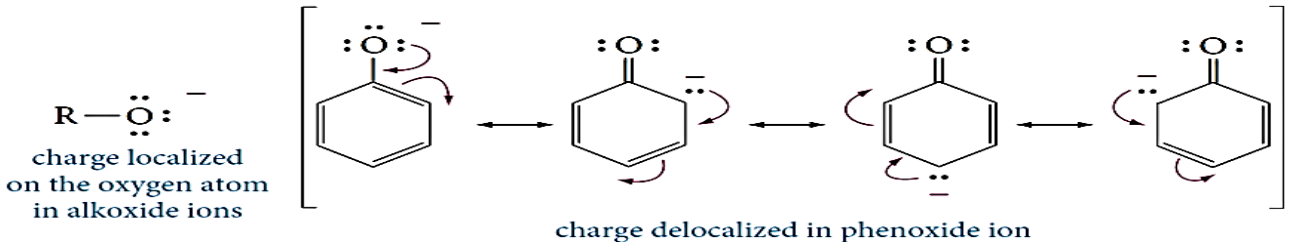
Like water, alcohols and phenols are weak acids.

The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water



Phenols are stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance.

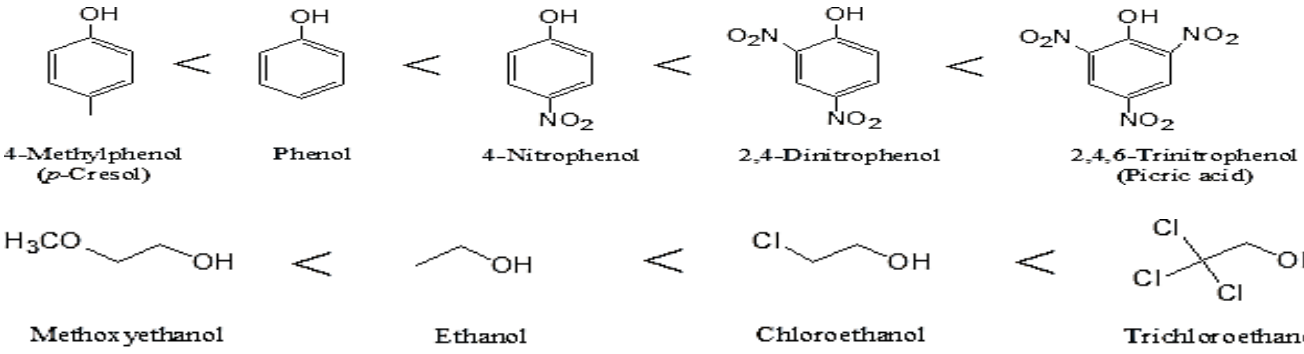
الفينولات اكثر حامضية من الكحولات لان الاكسجين الموجودة في الهيدروكسيل في الفينول تدخل في الرنين الخاص بحلقة البنزين ولذلك تكون مرتبطة بقوة مع الحلقة ويسهل عليها فقل الهيدروجين



All **electron-withdrawing groups increase aci**dity by stabilizing the conjugate base. **Electron-donating groups decrease acidity** because they destabilize the conjugate base.

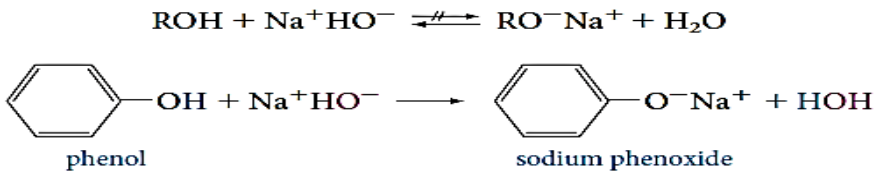
الكحولات الاولية اكثر حمضية من الثانوية والثالثية بسبب مجموعة ال R من المجموعات الطاردة للالكترونات فتقلل الحمضية

وتزداد الحمضية بوجود مجموعات ستحبة للالكترونات مثل الهلوجينات F , Cl ,Br



Alkoxides, the conjugate bases of alcohols, can be prepared by the reaction of an alcohol with sodium or potassium metal.

لا يتفاعل الكحول مع هيدروكسيد الصويوم ولكن يتفاعل الفينول لانة اكثر حمضية

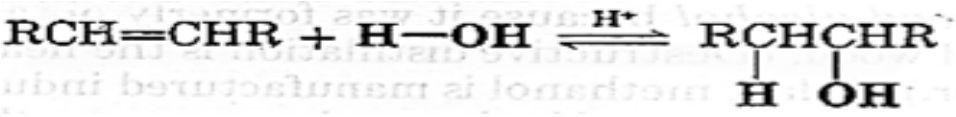


Preparation of Alcohols

From Alkenes

A. Hydration of Alkenes

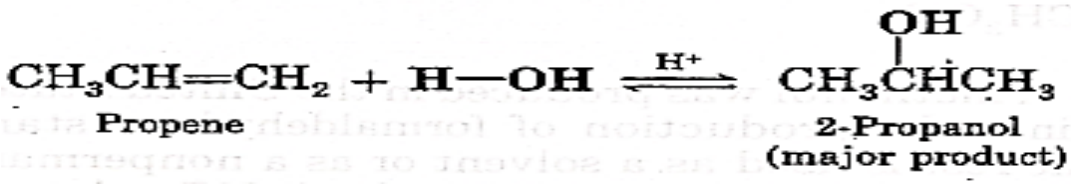
1. Addition of water to a double bond in the presence of an *acid catalyst, H^+*.



تكسر الرابطة الثائية ويتم اضافة الماء

طبقا لقاعدة ماركينيكوف

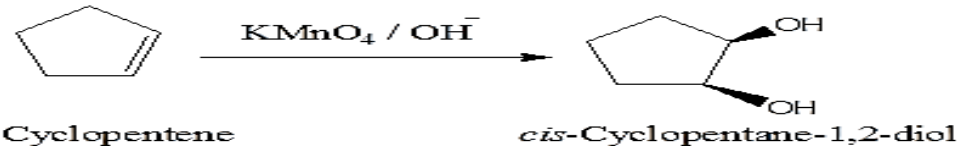
2. The addition follows *Markovnikov's rule.*



3. *It is not possible to prepare primary alcohols* except Ethanol.

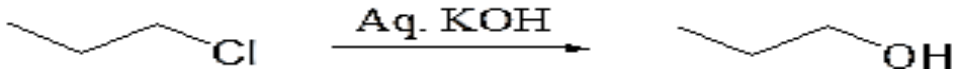
B. Oxidation of Cycloalkenes

Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).



اكسدة الالكين الحلقي تسكر الربطة وتدخل مجموعتين هيدروكسيل في الوضع سيس

Nucleophilic Substitution of Alkyl Halide

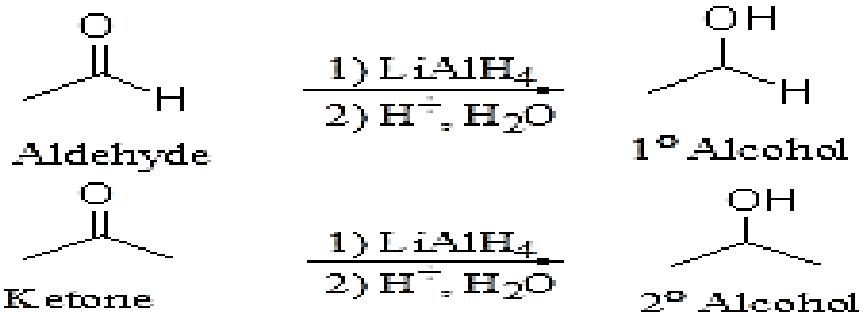


استبدال Xبمجموعة هيدروكسيل باستخدام

Aq KOH

Reduction of Ketones, and Aldehydes

Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.



اختزال الالدهيد والكيتون باستخدام اي من العوامل المختزلة مثل

Li Al H 4/ dry ether

Zn /H+ or Fe / HCl

Na /alcohol === NaBH4/ H2O

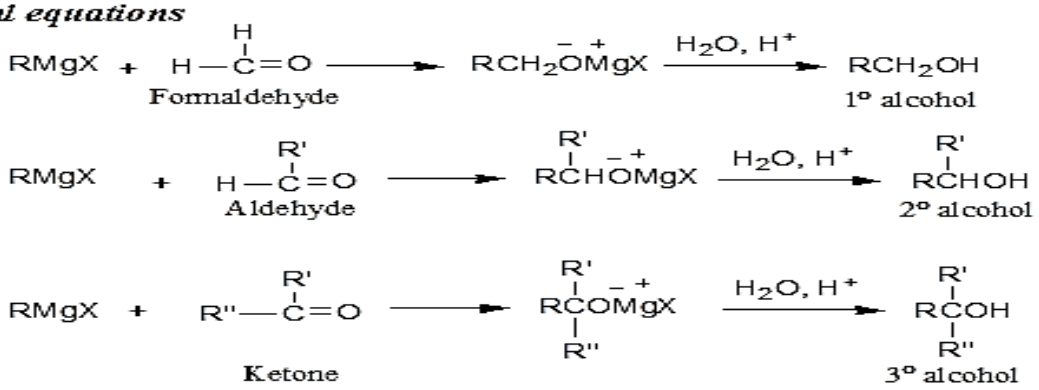
H2/ Pt or Pd |or Ni

اختزال الالدهيد يعطي كحول اولي

واختزال الكيتون يعطي كحول ثانوي

*A*ddition of Grignard's Reagent to Aldehydes and Ketones

General equations



يضاف قرينارد على مجموعة الكربونيل ودائما يزود Rعلى المركب وتفاعل قرينارد يتبع بإضافة ماء

Reactions of Alcohols and Phenols

Alcohols undergo two kinds of reactions:

Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

Those that involve the rupture of the carbon-oxygen bond (C-OH).

Phenols do not participate in reactions where the C-OH bond is broken.

تفاعلات الكحول تعتمد على كسر الرابطة بين الكربون والهيدروكسيل لكن من الصعب هذا مع الفينول

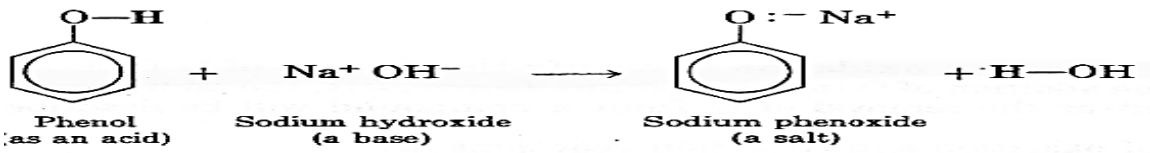
Reactions of Alcohols

A) Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

1) Reactions of Alcohols and Phenols as Acids: Salt Formation.

$$R{-}OH + Na^+ OH^- \longrightarrow \text{No reaction}$$

$$2\,CH_3O{-}H + 2\,Na \longrightarrow \underset{\text{Sodium methoxide}}{2\,CH_3O{:}^-\,Na^+} + H_2\uparrow$$
Methanol



B) Those that involve the rupture of the carbon-oxygen bond (C-OH).

The Reaction of Alcohols with Hydrogen Halides: Alkyl Halides

Alcohols react with hydrogen halides (HCl, HBr and HI) to give alkyl halides.

$$\underset{\text{alcohol}}{R{-}OH} + H{-}X \longrightarrow \underset{\text{alkyl halide}}{R{-}X} + H{-}OH$$

تفاعل استبدال ال OH ب X

Dehydration of Alcohols: Formation of Alkenes

Alcohols can be dehydrated by heating them with strong acid.

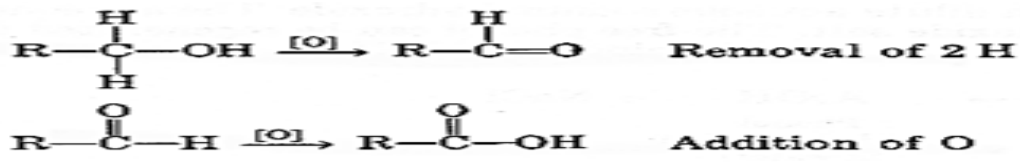
$$\underset{\text{ethanol}}{H{-}CH_2CH_2{-}OH} \xrightarrow{H^+,\,180^\circ C} \underset{\text{ethylene}}{CH_2{=}CH_2} + H{-}OH$$

نزع ماء من الكحول بالتسخين في وجود حمض قوي

يتكون الالكين

C) Oxidation Reactions

Oxidation is the removal of H from a compound and/or the addition of O to a compound.



الاكسدة هي نزع 2H

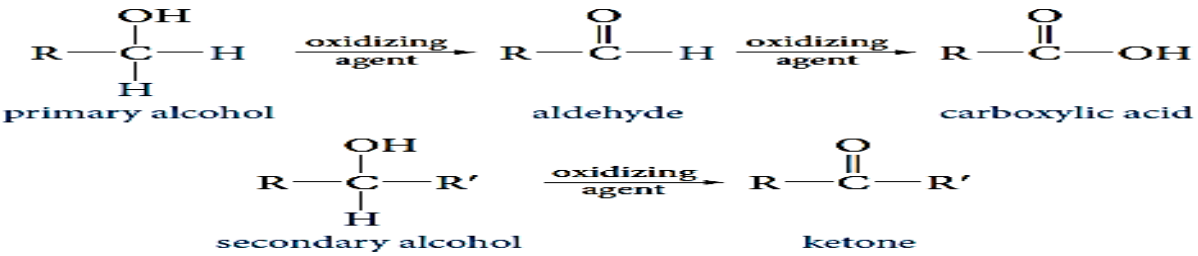
او إضافة O

An oxidizing agent is the chemical reagent that does the oxidation.

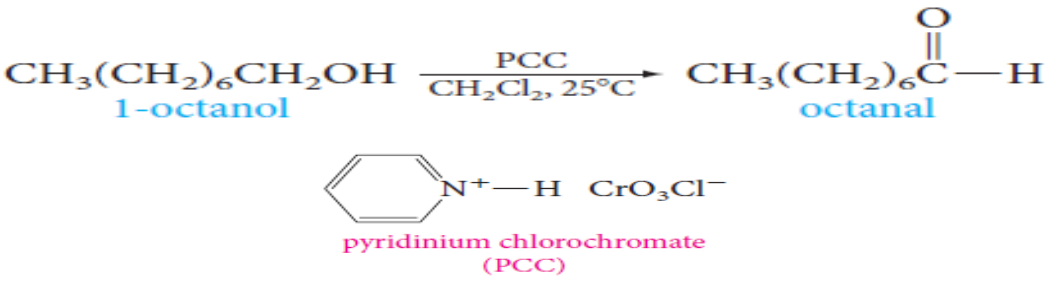
Primary alcohols give aldehydes, which may be further oxidized to carboxylic acids.

Secondary alcohols give ketones.

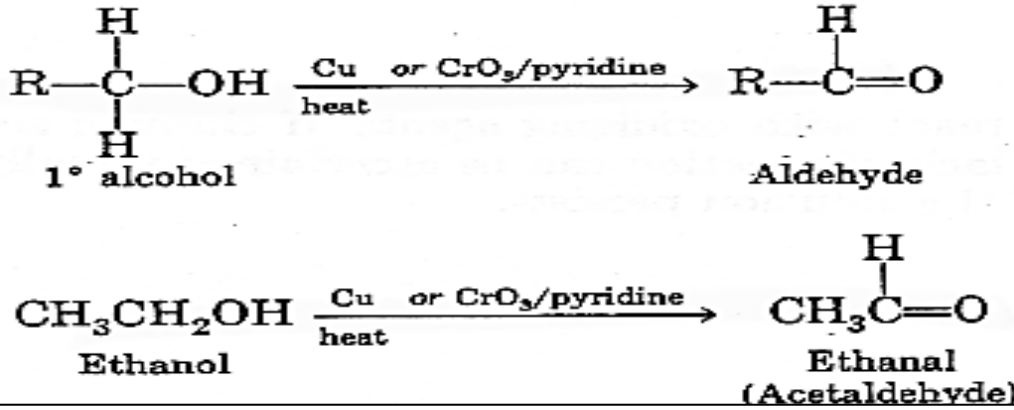
Tertiary alcohols, having no hydrogen atom on hydroxyl-bearing carbon, **do not undergo oxidation.**



Primary alcohols, oxidation can be stopped at aldehyde stage by special reagents, such as "pyridinium chlorochromate (PCC)".



Primary alcohols yield aldehydes when treated with *mild* oxidizing agents such as hot metallic copper or CrO_3 in pyridine.

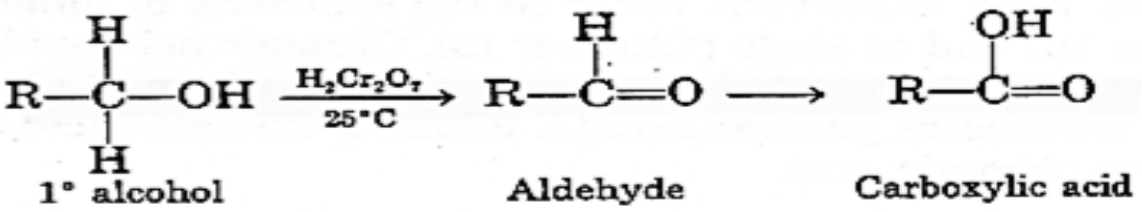


يتأكسد الكحول الاولي باستخدام عامل مؤكسد ضعيف الى الدهيد ولكن عند استخدام عامل مؤكسد قوي مثل K2Cr2O7 or KMnO4 الى حمض كربوكسيلي

CH2OH → CHo

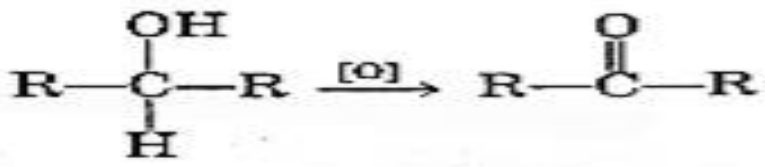
CH2OH → COOH

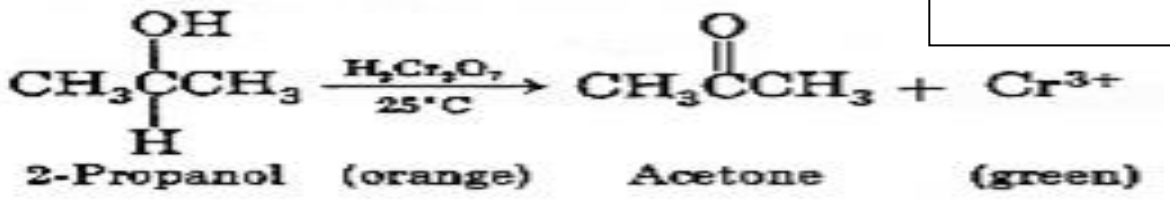
Primary alcohols yield aldehydes when treated with *stronger oxidizing agents*, such as chromic acid, $H_2Cr_2O_7$, or neutral potassium permanganate, $KMnO_4$, the intermediate aldehydes formed initially are oxidized further to carboxylic acids.



Secondary alcohols, when treated with *any* of the oxidizing agents mentioned previously, yield ketones.

الكحول الثانوي يتأكسد بأي عامل مؤكسد الى كيتون في حين لايتأكسد الكحول الثالثي بأي عامل مؤكسد





Preparation of Phenols

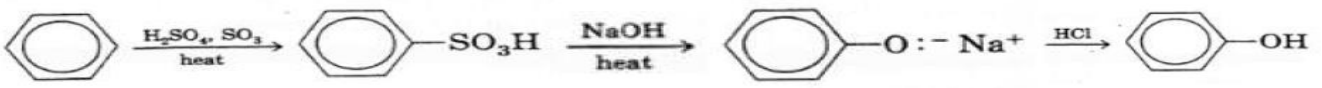
The Alkali Fusion of Sulfonates

The alkali fusion of sulfonates involves the following steps;

1. **Sulfonation** of an aromatic ring.

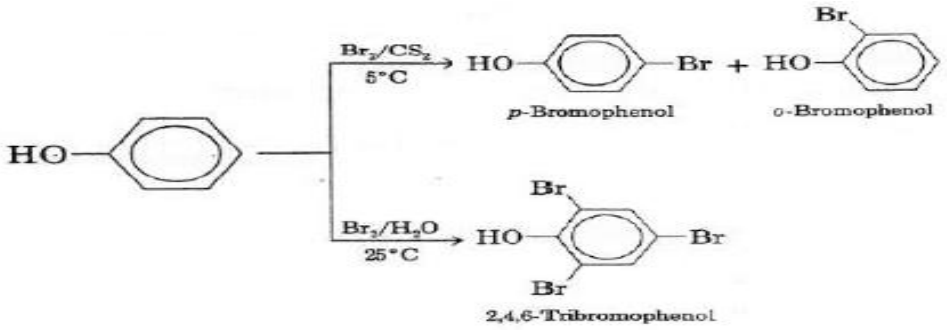
2. **Melting (fusion)** of the aromatic sulfonic acid with sodium hydroxide to give a phenoxide salt.

3. **Acidification** of the phenoxide with HCl to produce the phenol.



Reactions of Phenols

Halogenation takes place *without catalyst.*



على حسب نوع المذيب

The products depend on the solvent used.

In *aprotic solvents (*solvents that do not release protons) (CCl_4, CS_2)-bromination gives a mixture of *o*- and *p*-bromophenol.

In *protic solvents (solvents that can release protons)* (H_2O)-halogenation gives a trisubstituted phenol is produced.

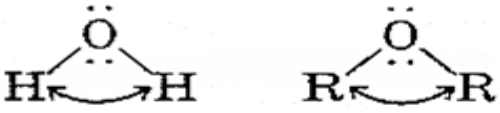
Ethers

Structure of Ethers

All **ethers** are compounds in which two organic groups are connected to a single oxygen atom.

The **general formula for an ether is R-O-R'**, where R and R' may be identical or different, and they may be alkyl or aryl groups

R—O—R, Ar—O—R, or Ar—O—Ar



The geometry of simple ethers is similar to that of water.

The ether is classified as

ايثرات متماثلة

Symmetrical ethers; When the organic groups attached to the oxygen are identical.

Unsymmetrical ethers (mixed ethers);

ايثرات غير متماثلة

When the organic groups attached to the oxygen are different.

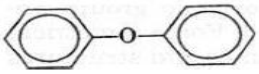
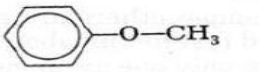
Nomenclature of Ethers

Common Names

Ethers are usually named by giving the name of each alkyl or aryl group, in alphabetical order, followed by the word *ether*

نكتب اسم المجموعة اذا كان متماثل ونكتب كلمة ايثر او يجوز كتابة ثنائي قبل الالكيل

في حالة الايثرات الغير متماثلة تكتب المجموعات مرتبة ابجديا ثم كلمة ايثر .

Methyl ether	$CH_3—O—CH_3$	Ethyl methyl ether	$CH_3—O—CH_2CH_3$
Ethyl ether	$CH_3CH_2—O—CH_2CH_3$	Ethyl-*n*-propyl ether	$CH_3CH_2—O—CH_2CH_2CH_3$
Vinyl ether	$CH_2=CH—O—CH=CH_2$	*t*-Butyl methyl ether	$(CH_3)_3C—O—CH_3$
Phenyl ether		Methyl phenyl ether (anisole)	

IUPAC System

تسمى الايثرات المعقدة طبقا لنظام الايوباك ونعتبر oR كفرع ويحدد مكانه وسم الاب هو اطول سلسلة لدينا

For ethers with more complex structures, it may be necessary to name the -OR group as an alkoxy group. In the IUPAC system, the smaller alkoxy group is named as a substituent.

$CH_3CH_2CH_2\underset{\displaystyle OCH_3}{\underset{\vert}{C}}HCH_3$	$CH_3CH_2CH_2\underset{\displaystyle OCH_2CH_3}{\underset{\vert}{C}}HCH_2CH_3$	$H_3CO—CH_2CH_2OH$
2-Methoxypentane	3-Ethoxyhexane	2-Methoxyethanol

Physical Properties of Ethers

Physical State

Ethers are colorless compounds with characteristic, relatively pleasant odors.

Boiling Points

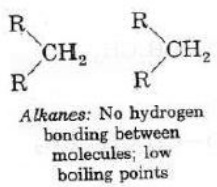
لا تستطيع تكوين روابط هيدروجينية بين جزيئاتها ولذك درجة غليانها منخفضة وتزداد بزيادة الوزن الجزيئي

They have lower boiling points (bp,s) than alcohols with an equal number of carbon atoms.

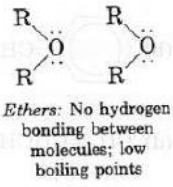
In fact, an ether has nearly the same bp as the corresponding hydrocarbon in which a $-CH_2-$ group replaces the ether's oxygen. ☐

Because of their structures (no O-H bonds), ether molecules ***cannot form hydrogen bonds*** *with one another.* ☐

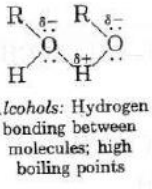
تستطيع اليثرات تكوين روابط هيدروجينية مع الماء



Alkanes: No hydrogen bonding between molecules; low boiling points



Ethers: No hydrogen bonding between molecules; low boiling points



Alcohols: Hydrogen bonding between molecules; high boiling points

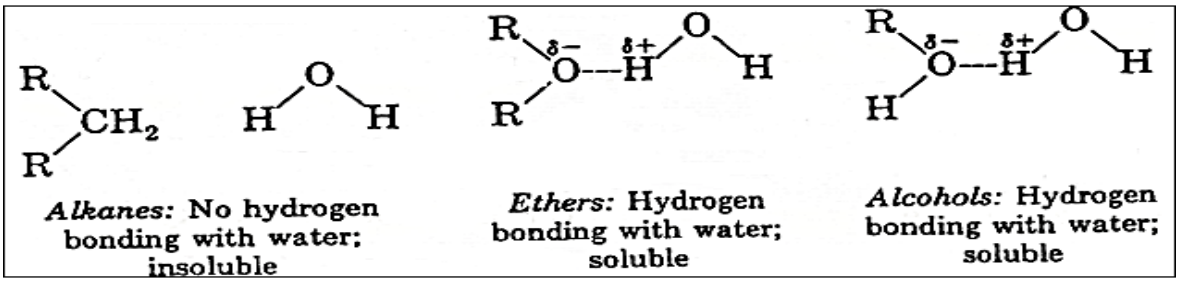
Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

Solubility

الايثرات مركبات ضعيفة القطبية وتذوب بقلة فى الماء

Low-molecular-weight ethers, such as dimethyl ether, are quite soluble in water.

Ether molecules can form hydrogen bonds to water.



Alkanes: **No hydrogen bonding with water; insoluble**

Ethers: **Hydrogen bonding with water; soluble**

Alcohols: **Hydrogen bonding with water; soluble**

Preparation of Ethers

There are *two general methods* for synthesizing ethers.

1) Dehydration of alcohols

تستخدم هذه الطريقة لتحضير الايثرات المتماثلة سبق ذكرها

It is used commercially and in the laboratory to make certain symmetrical ethers.

It takes place in the presence of acid catalysts (H_2SO_4, H_3PO_4) (intermolecular reaction)

$$R—OH + H—OR \xrightarrow[\text{heat}]{H^+} R—O—R + H_2O$$

Example;

The most important commercial ether is diethyl ether. It is prepared from ethanol and sulfuric acid.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + HOCH_2CH_3 \xrightarrow[140°C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2O$$

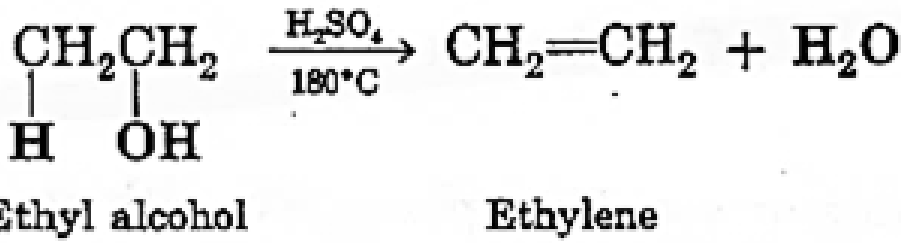
2) Williamson synthesis

تستخدم في تحضير الايثرات المتماثلة والغير متماثلة بإضافة الكوكسيد او فينوكسيد الى هاليد الالكيل الأولية وهو تفاعل استبدال

General laboratory method used to prepare all kinds of ethers, symmetrical and unsymmetrical.

Scope and Limitations

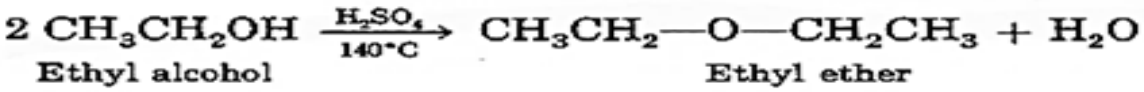
When ethyl alcohol is dehydrated by sulfuric acid at 180° C, the dominant product is ethylene.



To prepare ethyl ether

Dissolve ethyl alcohol in sulfuric acid at ambient temperature.

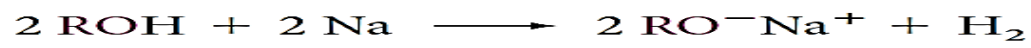
Heat the solution to 140°C while adding more alcohol.



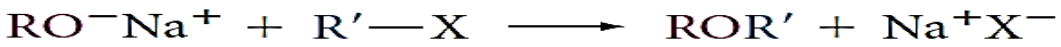
2) Williamson Synthesis

This method has two steps;

1) An alcohol is converted to its alkoxide by treatment with a reactive metal (sodium or potassium).



2) Displacement is carried out between the alkoxide and an alkyl halide.



To obtain the best yields of mixed dialkyl ethers, we select a 1° rather than a 2°or 3°alkyl halide and react it with a sodium alkoxide

To prepare an alkyl aryl ether, we must be careful not to pick a combination in which one of the reagents has a halogen directly attached to an aromatic ring.

Example 1; Preparation of *t*-butyl methyl ether, $(CH_3)_3C\text{-}O\text{-}CH_3$.

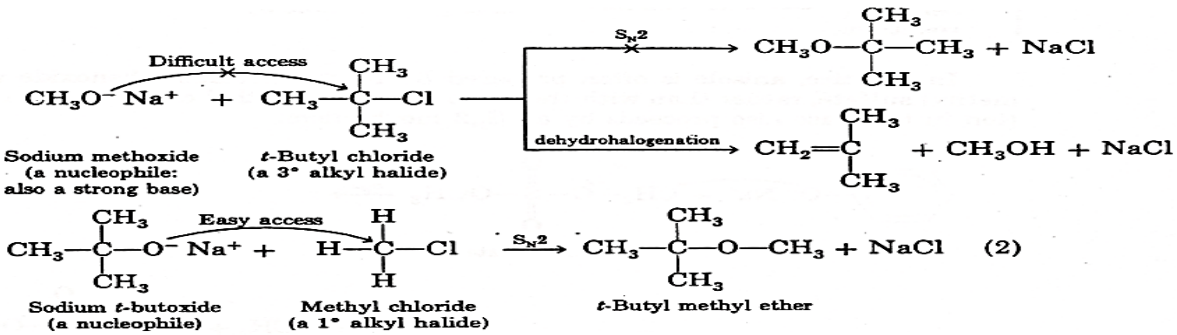
In theory, this could be done by either of two reactions.

1. You could react sodium methoxide, $CH_3O^-Na^+$, with *t*-butyl chloride, $(CH_3)_3C\text{-}Cl$.

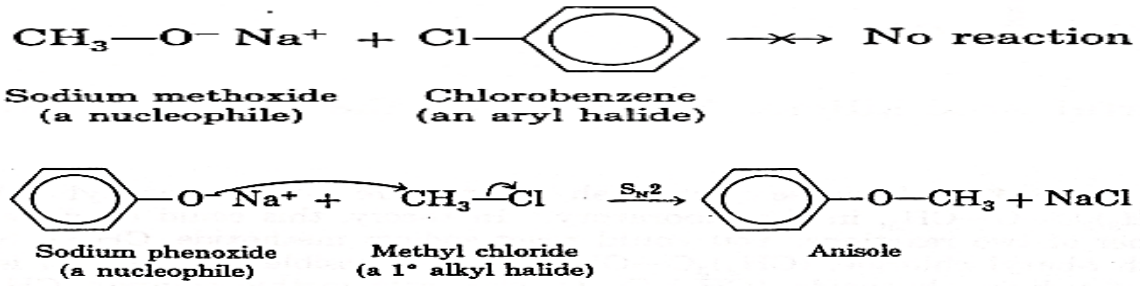
This combination leads to dehydrohalogenation to an alkene, an elimination reaction.

2. You could react sodium *t*-butoxide, $(CH_3)_3C\text{-}O^-Na^+$, with methyl chloride, CH_3Cl.

This route gives the desired ether by substitution.



Example 2; Assume you need to synthesize methyl phenyl ether (anisole), $CH_3\text{-}O\text{-}C_6H_5$, by the Williamson method. *In theory, you could obtain anisole in either of two ways.*



Reactions of Ethers

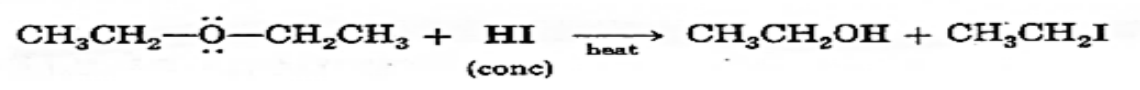
Ethers are quite stable compounds.

The **ether** linkage does not react with bases, reducing agents, oxidizing agents, or active metals.

Ethers react only under strongly acidic conditions.

Cleavage of Ethers by Hot Concentrated Acids

When **ethers** are heated in concentrated acid solutions, the ether linkage is broken.



The acids most often used in this reaction are HI, HBr, and HCl.

If an *excess of acid* is present, the alcohol initially produced is converted into an alkyl halide by the reaction.

$$R—OH + HX \longrightarrow RX + H_2O$$

For example,

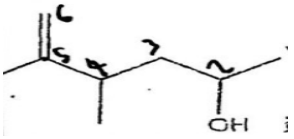
$$CH_3CH_2—O—CH_2CH_3 + 2\,HBr \xrightarrow[\text{(conc)}]{\text{heat}} 2\,CH_3CH_2Br + H_2O$$

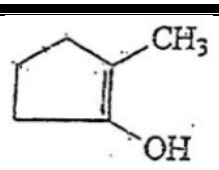
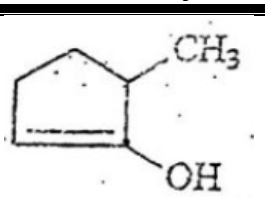
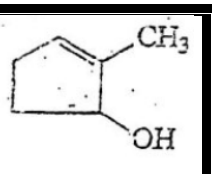
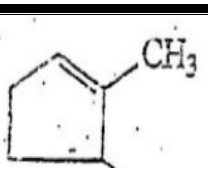
تتفاعل الايثرات مع الاحماض الهالوجينية مثل HCl , HBr , HI

اذا تفاعل واحد مول من الحمض الهلوجيني مع الايثر تعطي هاليد الالكيل وكحول

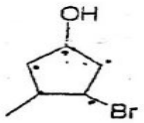
اما اذا تفاعل 2 مول يعطي2 جزء هاليد الالكيل وجزء ماء

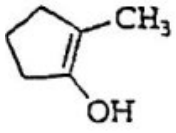
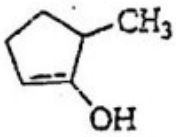
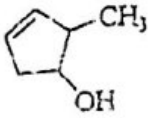
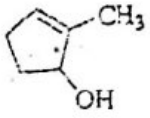
1	The common name of 2- propenol						
A	Allyl alcohol	b	Tert-butyl alcohol	c	Isopropyl alcohol	d	Vinyl alcohol

2	*The name of the following compound is:* 		
A	2,3-dimethyl-1- hexen-5-ol	b	4-propenyl-2-pentanol
c	4,5-Dimethyl-5-hexen-2-ol	d	5-hydroxy-2,3-dimethyl-1-hexene

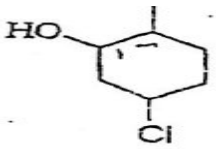
3	The structural formula of 5-methyl-1-cyclopentenol is?						
A		b		c		d	

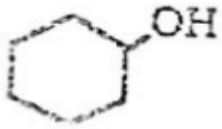
4	How many hydroxyl group does ethylene glycol have ?						
A	one	b	two	c	three	d	four

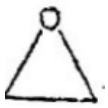
5	The IUPAC name of the following compound is 		
A	1-Bromo-4-hydroxy-2-methylcyclopentane	b	4-Bromo-3-methylcyclopentan-1-ol
c	3-Bromo-4-methylcyclopentanol	d	2-Bromo-3-methylcyclopentanol

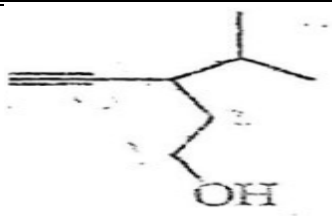
6	The structure of 2-methyl-2-cyclopentenol is:						
A		b		c		d	

7	The IUPAC name of tert-butyl alcohol is:						
A	2-propanol	b	2-butanol	c	2-methyl-2-propanol	d	1-butanol

8	The IUPAC name of  is:		
A	2-chloro-6-methylcyclohexanol	b	3-chloro-6-methylcyclohexanol
c	5-chloro-2-methylcyclohexanol	d	2-chloro-5-methylcyclohexanol

9	The IUPAC name of  is:		
A	phenol	b	Hexanol
c	Cyclohexane alcohol	d	Cyclohexyl alcohol

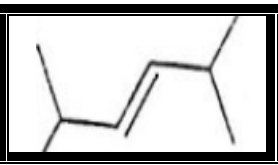
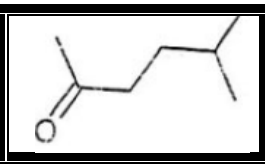
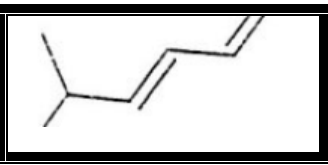
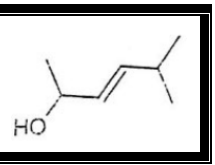
10	*Which one form the following does not has the ability to form interamolecuar H-bond ?*						
A	$CH_3CH_2CH_2CH_2OH$	b		c	CH_3CHCH_2OH CH_3	d	

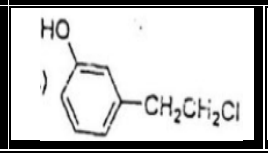
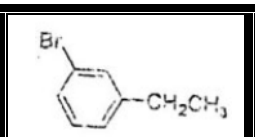
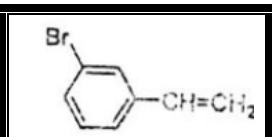
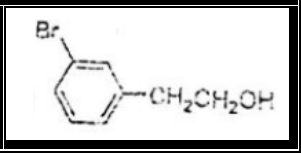
11	**The IUPAC name of the following compound is** 		
A	**3-Acetylene-4- methyl-1-pentanol**	**b**	**3- iso propyl-4-pentyn-1-ol**
c	**3-ethynyl-4-methyl-1-pentanol**	**d**	**3-isopropyl-1-pentyne-5-ol**

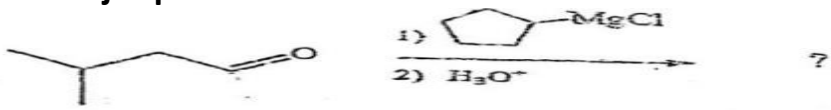
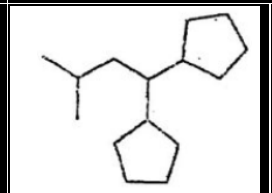
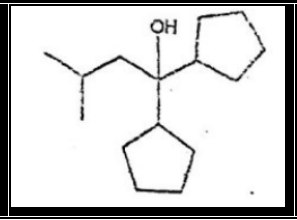
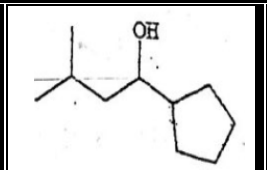
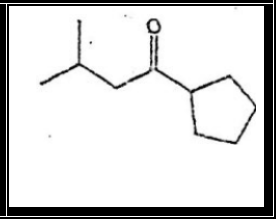
12	**The IUPAC name of the following compound is** 		
A	**2-chloro-5-hexanol**	**b**	**2-hydroxy-5-chlorohexane**
c	**2-chloro-5-hydroyhexane**	**d**	**5-choro-2- hexanol**

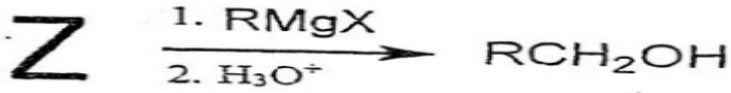
13	**Which of the following has highest boiling point ?**						
A	**butanol**	**b**	**Ethyl boromide**	**c**	**Dimethyl ether**	**d**	**methanol**
14	***Which of the following compounds is more soluble in water?***						
A	**propanol**	**b**	**Diethyl ether**	**c**	**hexane**	**d**	**benzene**

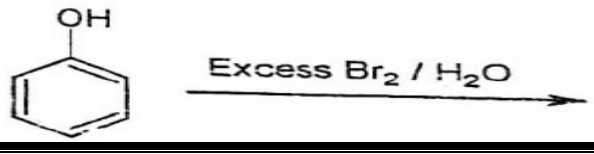
15	**The product of the following reaction is** 

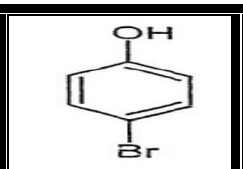
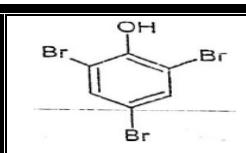
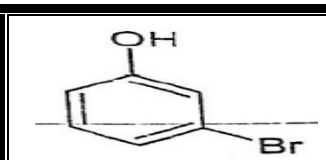
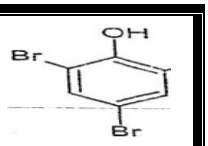
A		b		c		d	

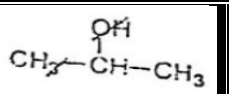
16	**The product of the following reaction is** 						
A		b		c		d	

17	**The major product of this reaction is ?** 						
A		b		c		d	

18	**The following general equation, the reagen Z is** 						
A	**Acetone**	b	**Methanol**	c	**formaldhyde**	d	**Acetaldehyde**

19	***The product of the following reaction***  **is :**						

A		b		c		d	

20	Which of the following is the most acidic compound?						
A	$CH_3\text{-}CH_2\text{-}CH_2\text{—}OH$	b		c	Phenol	d	*p*-Nitrophenol

Key answer

السؤال	الاجابة	السؤال	الاجابة
1	B	11	B
2	C	12	D
3	B	13	A
4	B	14	A
5	B	15	D
6	D	16	D
7	C	17	C
8	B	18	C
9	D	19	B
10	B	20	D