AL- MUSTAQBAL UNIVERSITY

College Of Health And Medical Techniques

Prosthetic Dental Techniques Department

Second Grade

Second Semester

Advanced chemistry

Lecture 12 (The theoretical part)

(Organic compounds (ALKYNES))

By:

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ALKYNES

Hydrocarbons that contain a carbon–carbon triple bond are called **alkynes.** Noncyclic alkynes have the molecular formula C_nH_{2n-2}. *Acetylene* ($HC\equiv CH$) is the simplest alkyne. We call compounds that have their triple bond at the end of a carbon chain ($RC\equiv CH$) *monosubstituted,* or *terminal, alkynes.* Disubstituted alkynes ($RC\equiv CR_-$) are said to have *internal* triple bonds. You will see in this chapter that a carbon – carbon triple bond is a functional group, reacting with many of the same reagents that react with the double bonds of alkenes.
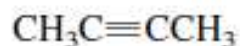
8.3.1. NOMENCLATURE

In naming alkynes the usual IUPAC rules for hydrocarbons are followed, and the suffix *-ane* is replaced by *-yne.* Both acetylene and ethyne are acceptable IUPAC names for $HC\equiv CH$. The position of the triple bond along the chain is specified by number in a manner analogous to alkene nomenclature.

$HC\equiv CCH_3$	$HC\equiv CCH_2CH_3$	$CH_3C\equiv CCH_3$	$(CH_3)_3CC\equiv CCH_3$
Propyne	1-Butyne	2-Butyne	4,4-Dimethyl-2-pentyne

Alkynes resemble alkanes and alkenes in their physical properties. They share with these other hydrocarbons the properties of low density and low water-solubility. They are slightly more polar and generally have slightly higher boiling points than the corresponding alkanes and alkenes.

8.3.2. SUMMARY

1-Alkynes are hydrocarbons that contain a carbon–carbon *triple bond.* Simple alkynes having no other functional groups or rings have the general formula C_nH_{2n-2}. Acetylene is the simplest alkyne.

2-Alkynes are named in much the same way as alkenes, using the suffix -yne instead of -ene.
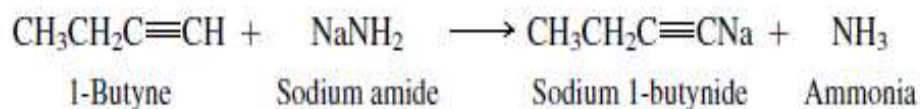
4,4-Dimethyl-2-pentyne

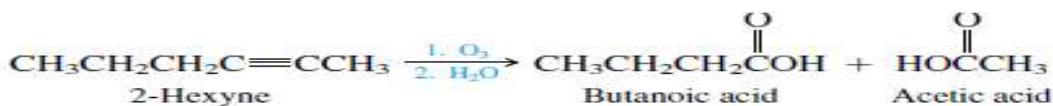3-The physical properties (boiling point, solubility in water, dipole

moment) of alkynes resemble those of alkanes and alkenes.

4-Acetylene is linear and alkynes have a linear geometry of their $X{-}C{\equiv}C{-}Y$ units. The carbon–carbon triple bond in alkynes is composed of a _ and two components. The triply bonded carbons are *sp* hybridized. The _ component of the triple bond contains two electrons in an orbital generated by the overlap of *sp*-hybridized orbitals on adjacent carbons. Each to these carbons also has two $2p$ orbitals, which overlap in pairs so as to give two л orbitals, each of which contains two electrons.

5-Acetylene and terminal alkynes are more *acidic* than other hydrocarbons. They have a Ka's for ionization of approximately 10^{-26}, compared with about 10^{-45} for alkenes and about 10^{-60} for alkanes. Sodium amide is a strong enough base to remove a proton from acetylene or a terminal alkyne, but sodium hydroxide is not.

$$CH_3CH_2C{\equiv}CH + NaNH_2 \longrightarrow CH_3CH_2C{\equiv}CNa + NH_3$$

| 1-Butyne | Sodium amide | Sodium 1-butynide | Ammonia |

6-Carbon–carbon triple bonds can be cleaved by ozonolysis. The cleavage products are carboxylic acids.

$$CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH + HO\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

| 2-Hexyne | | Butanoic acid | Acetic acid |

9. ALCOHOLS AND ALKYL HALIDES

In this chapter we begin our discussion of organic chemical *reactions* by directing attention to *alcohols* and *alkyl halides*. These two rank among the most useful classes of organic compounds because they often serve as starting materials for the preparation of numerous other families. Two reactions that lead to alkyl halides will be described in this chapter. Both illustrate functional group transformations. In the first, the hydroxyl group of an alcohol is replaced by halogen on treatment with a hydrogen halide.

$$R{-}OH + H{-}X \longrightarrow R{-}X + H{-}OH$$

| Alcohol | Hydrogen halide | Alkyl halide | Water |
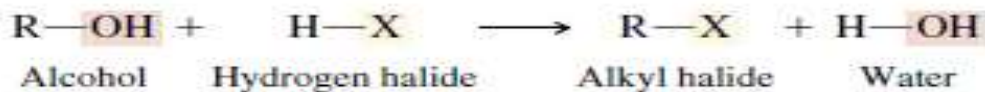
In the second, reaction with chlorine or bromine causes one of the hydrogen substituents of an alkane to be replaced by halogen.
Both reactions are classified as *substitutions*, a term that describes the relationship

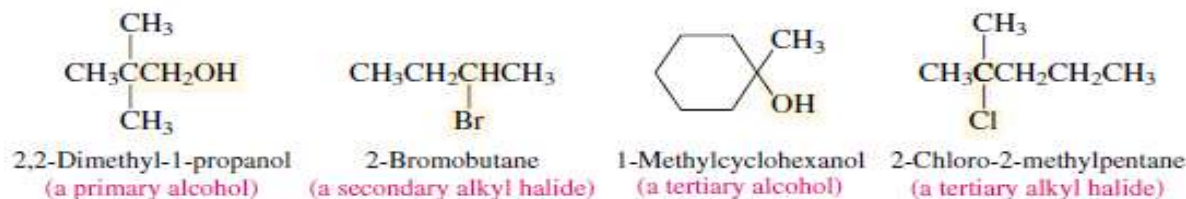between reactants and products—one functional group replaces another. each reaction. A **mechanism** attempts to show *how* starting materials are converted into products during a chemical reaction.

While developing these themes of reaction and mechanism, we will also use alcohols and alkyl halides as vehicles to extend the principles of IUPAC nomenclature, continue to develop concepts of structure and bonding.

9.1. IUPAC NOMENCLATURE OF ALKYL HALIDES

The IUPAC rules permit alkyl halides to be named in two different ways, called *functional class* nomenclature and *substitutive* nomenclature. In **functional class nomenclature** the alkyl group and the halide (*fluoride, chloride, bromide,* or *iodide*) are designated as separate words. The alkyl group is named on the basis of its longest continuous chain beginning at the carbon to which the halogen is attached.

| CH_3F | $CH_3CH_2CH_2CH_2CH_2Cl$ | $CH_3CH_2CHCH_2CH_2CH_3$ | |
| ethyl fluoride | Pentyl chloride | 1-Ethylbutyl bromide | Cyclohexyl iodide |

When the carbon chain bears both a halogen and an alkyl substituent, the two substituents are considered of equal rank, and the chain is numbered so as to give the lower number to the substituent nearer the end of the chain.

Substitutive names are preferred, but functional class names are sometimes more convenient or more familiar and are frequently encountered in organic chemistry.

9.1.2. IUPAC NOMENCLATURE OF ALCOHOLS

Functional class names of alcohols are derived by naming the alkyl group that bears the hydroxyl substituent (±OH) and then adding *alcohol* as a separate word. The chain is always numbered beginning at the carbon to which the hydroxyl group is attached.

Substitutive names of alcohols are developed by identifying the longest continuous chain that bears the hydroxyl group and replacing the -e ending of the corresponding alkane by the suffix *-ol.* The position of the hydroxyl group is indicated by number, choosing the sequence that assigns the lower locant to the carbon that bears the hydroxyl group.

	CH_3CH_2OH	$CH_3CHCH_2CH_2CH_2CH_3$	$CH_3CCH_2CH_2CH_3$
Functional class name:	Ethyl alcohol	1-Methylpentyl alcohol	1,1-Dimethylbutyl alcohol
Substitutive name:	Ethanol	2-Hexanol	2-Methyl-2-pentanol

Hydroxyl groups take precedence over ("outrank") alkyl groups and halogen substituents in determining the direction in which a carbon chain is numbered.

7 6 5 4 3 2 1
$CH_3CHCH_2CH_2CHCH_2CH_3$
| |
CH_3 OH

6-Methyl-3-heptanol
(not 2-methyl-5-heptanol)

trans-2-Methylcyclopentanol

$FCH_2CH_2CH_2OH$

3-Fluoro-1-propanol

9.2. CLASSES OF ALCOHOLS AND ALKYL HALIDES

Alcohols and alkyl halides are classified as primary, secondary, or tertiary according to the classification of the carbon that bears the functional group. Thus, *primaryalcohols* and *primary alkyl halides* are compounds of the type RCH_2G (where G is the functional group), *secondary alcohols* and *secondary alkyl halides* are compounds of the type R_2CHG, and *tertiary alcohols* and *tertiary alkyl halides* are compounds of the type R_3CG.

CH_3
|
CH_3CCH_2OH
|
CH_3

2,2-Dimethyl-1-propanol
(a primary alcohol)

$CH_3CH_2CHCH_3$
|
Br

2-Bromobutane
(a secondary alkyl halide)

CH_3

OH

1-Methylcyclohexanol
(a tertiary alcohol)

CH_3
|
$CH_3CCH_2CH_2CH_3$
|
Cl

2-Chloro-2-methylpentane
(a tertiary alkyl halide)

Many of the properties of alcohols and alkyl halides are affected by whether their functional groups are attached to primary, secondary, or tertiary carbons. We will see a number of cases in which a functional group attached to a primary carbon is more reactive than one attached to a secondary or tertiary carbon, as well as other cases in which the reverse is true.
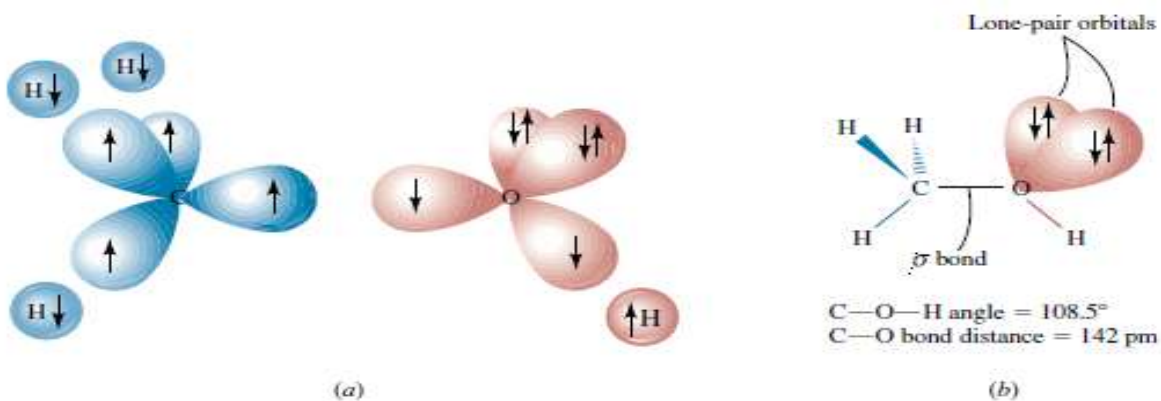

Lone-pair orbitals

C—O—H angle = 108.5°
C—O bond distance = 142 pm

(a)   (b)

FIGURE 23 Orbital hybridization model of bonding in methanol. (*a*) The orbitals used in bonding are the 1*s* orbitals of hydrogen and *sp*3- hybridized orbitals of

carbon and oxygen. (*b*) The bond angles at carbon and oxygen are close to tetrahedral, and the carbon oxygen _ bond is about 10 pm shorter than a carbon–carbon single bond.

9.3.SUMMARY

Chemical reactivity and functional group transformations involving the preparation of alkyl halides from alcohols and from alkanes are the main themes of this chapter. Although the conversions of an alcohol or an alkane to an alkyl halide are both classified as substitutions, they proceed by very different mechanisms.

1-Alcohols and alkyl halides may be named using either **substitutive** or **functional class** nomenclature. In substitutive nomenclature alkyl halides are named as halogen derivatives of alkanes. The parent is the longest continuous chain that bears the halogen substituent, and in the absence of other substituents the chain is numbered from the direction that gives the lowest number to the carbon that bears the halogen. The functional class names of alkyl halides begin with the name of the alkyl group and end with the halide as a separate word.

$CH_3CHCH_2CH_2CH_2CH_3$ Substitutive name: 2-Bromohexane
| Functional class name: 1-Methylpentyl bromide
Br
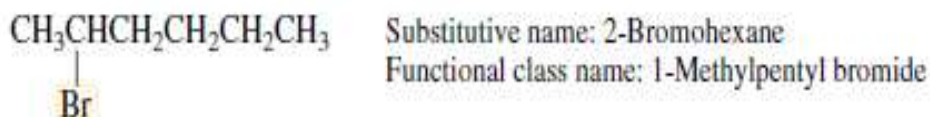
2-The substitutive names of alcohols are derived by replacing the -*e* ending of an alkane with -*ol*. Functional class names of alcohols begin with the name of the alkyl group and end in the word "alcohol."

$CH_3CHCH_2CH_2CH_2CH_3$ Substitutive name: 2-Hexanol
| Functional class name: 1-Methylpentyl alcohol
OH
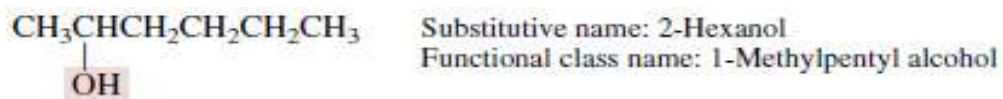
3-Alcohols (X = OH) and alkyl halides (X = F, Cl, Br, or I) are classified as primary, secondary, or tertiary according to the degree of substitution at the carbon that bears the functional group.

$$RCH_2X \qquad \underset{\overset{|}{X}}{RCHR'} \qquad \underset{\overset{|}{X}}{\overset{\overset{R''}{|}}{RCR'}}$$

Primary   Secondary   Tertiary

4-The halogens (especially fluorine and chlorine) and oxygen are more electronegative than carbon, and the carbon–halogen bond in alkyl halides and the carbon–oxygen bond in alcohols are polar. Carbon is the positive end of the dipole and halogen or oxygen the negative end.

5-Dipole/induced-dipole and dipole–dipole attractive forces make alcohols higher boiling than alkanes of similar molecular weight. The attractive force between ±OH groups is called **hydrogen bonding.**
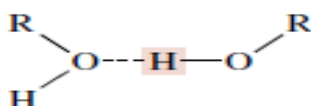
Hydrogen bonding between the hydroxyl group of an alcohol and water makes the water-solubility of alcohols greater than that of hydrocarbons. Low-molecular-weight alcohols [CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, and $(CH_3)_2CHOH$] are soluble in water in all proportions. Alkyl halides are insoluble in water.

6-**Brønsted acids** are proton donors; **Brønsted bases** are proton acceptors. Strong acids transfer protons to alcohols to form **alkyloxonium ions.** An alkyloxonium ion is the **conjugate acid** of an alcohol.

Alcohol
(base)

Alkyloxonium ion
(conjugate acid)

7-Proton transfer from a Brønsted acid to the oxygen of water is a single step process and is very fast. It is a bimolecular, concerted process.

8-Carbocations contain a positively charged carbon with only three atoms or groups attached to it. This carbon is *sp2*-hybridized and has a vacant *2p* orbital.

Carbocations are stabilized by alkyl substituents attached directly to the positively charged carbon. Alkyl groups are electron-releasing substituents. Stability increases in the order:

(least stable) $CH_3^+ < R_2CH^+ < R_3C^+$ (most stable)

Carbocations are strongly **electrophilic** (Lewis acids) and react with **nucleophiles** (Lewis bases).

9-The conversion of an alcohol to an alkyl halide on reaction with a hydrogen halide is a **nucleophilic substitution.** Nucleophilic substitutions (SN) are classified as SN^1 or SN^2 according to whether the rate-determining step is unimolecular or bimolecular.

10-The rates at which alcohols are converted to alkyl halides depends on the rate of carbocation formation: tertiary alcohols are most reactive; primary alcohols and methanol are least reactive.

11-Primary alcohols do not react with hydrogen halides by way of carbocation intermediates. The nucleophilic species (Br_) attacks the alkyloxonium ion and "pushes off" a water molecule from carbon in a bimolecular step. This step is rate-determining, and the mechanism is SN^2.

12-Methane reacts with Cl2 to give chloromethane, dichloromethane, trichloromethane, and tetrachloromethane.

13-Chlorination of methane, and halogenation of alkanes generally, proceed by way of **free-radical** intermediates. Alkyl radicals are neutral and have an unpaired electron on carbon.
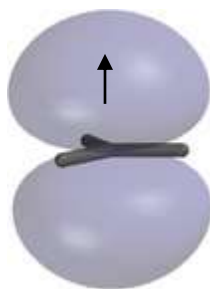
Like carbocations, free radicals are stabilized by alkyl substituents. The order of free-radical stability parallels that of carbocation stability.

وزارة التعليم العالي والبحث العلمي

كلية التقنيات الصحية والطبية

تقنيات التحليلات المرضية و صحة المجتمع

الكيمياء العامة / النظري

المرحلة الأولى

المحاضـــــرة العاشرة

Lecture (10)

(الكيمياء العضوية)

(Organic compounds)

- **SUMMARY**
- **CLASSES OF ALCOHOLS AND ALKYL HALIDES**
- **IUPAC NOMENCLATURE OF ALCOHOLS**
- **IUPAC NOMENCLATURE OF ALKYL HALIDES**
- ALCOHOLS AND ALKYL HALIDES
- **SUMMARY**
- NOMENCLATURE
- ALKYNES

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