

Organic 1



Subject: Aldehydes &
Ketones



Pharmaceutical Organic Chemistry-1

Chapter-5: Aldehydes & Ketones



کربونیل

Aldehydes & Ketones

Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
Ketones	$R-C(=O)-R'$	Aldehydes	$R-C(=O)-H$
Carboxylic acids	$R-C(=O)-OH$	Acid Chlorides	$R-C(=O)-Cl$
Esters	$R-C(=O)-O-R'$	Amides	$R-C(=O)-NH_2$

۱ از ۵
 R_1 : H یا R → اسید
 R_2 : N → کلراید

۱ از ۶
 R_1 : H یا R → اسید
 R_2 : Cl → کلراید

۱ از ۵
 R_1 یا H یا R → و استر
 R_2 : RO

۱ از ۵
 R_1 : H یا R → کربوکسیل
 R_2 : OH

۱ از ۵
 $R_1, R_2 \rightarrow H$ → الیفاتر
 R_1 : H, R_2 : C

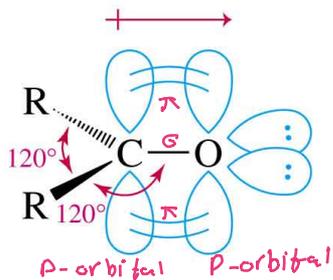
۱ از ۶
 $R_1, R_2 \rightarrow C$ → کیتون

Aldehydes & Ketones



- o Carbon is **sp² hybridized**. *o is sp² hybridized*
- o **C=O bond** is shorter, stronger, and more polar than C=C bond in alkenes.

	<i>length</i>	<i>energy</i>
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)



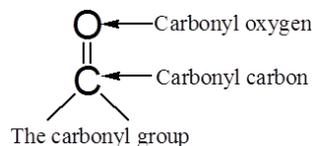
صورة

الدينامية

الرابطه الأقصر دائما أقوى
فبحتاج طاقة أعلى لكسرها

Structure of Aldehydes and Ketones

- o **Aldehydes and ketones** are characterized by the presence of the carbonyl group.



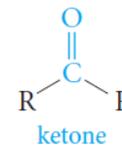
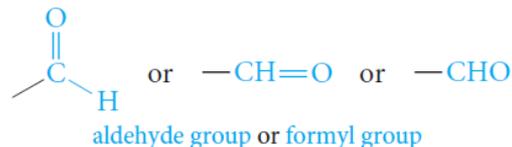
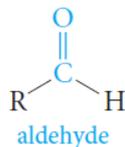
- o **Aldehydes** have at least one hydrogen atom attached to the carbonyl carbon atom.

The remaining group may be another hydrogen atom or any aliphatic or aromatic organic group.

The **-CH=O** group characteristic of aldehydes is often called a formyl group.



- o In **ketones**, the carbonyl carbon atom is connected to two other carbon atoms.



*
عسول R-COH
الدهايد R-CHO
فوق في
الاختصارات

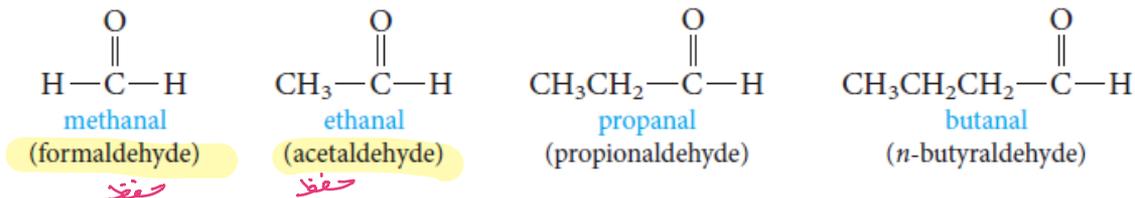
Nomenclature of Aldehydes

IUPAC

System

- Aliphatic aldehydes are named by dropping the suffix *-e* from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and replacing it with the suffix *-al*.

Alkane - e + al = Alkanal



Nomenclature of Aldehydes

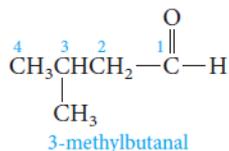
IUPAC

System

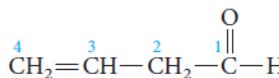
o **Substituted aldehydes**, we number the chain starting with the aldehyde carbon.

- **-CH=O group** is assigned the number **1 position**. ردائما ترقيم 1 للكربون
- Aldehyde group has priority over a double bond or hydroxyl group. (الكربونيل)

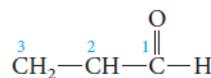
1- نختار اطول سلسلة تحتوي على مجموعة الكربونيل



3-methylbutanal



3-butenal



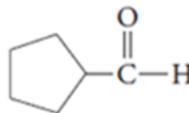
2,3-dihydroxypropanal (glyceraldehyde)

بما ان الكربونيل

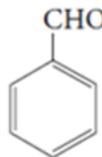
نختار السلسلة الأطول التي تحتوي على كربونيل ورابطة شاذية والأولوية بالترتيب للكربونيل

نختار اطول سلسلة تحتوي على

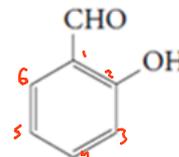
o **Cyclic aldehydes**, the suffix **-carbaldehyde** is used. كربونيل وOH والأولوية للكربونيل



formylcyclopentane (cyclopentancarbaldehyde)



benzaldehyde (benzaldehyde)



salicylaldehyde (2-hydroxybenzaldehyde)

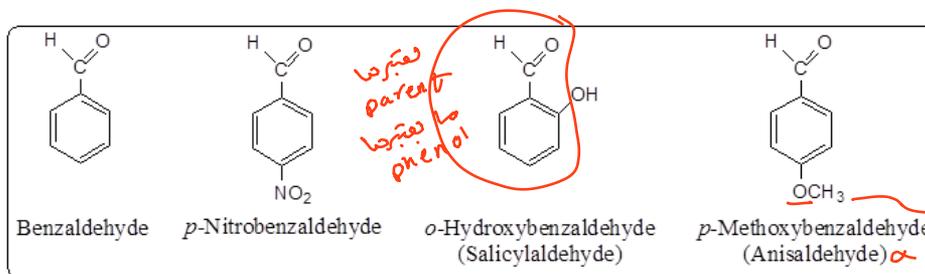
Common (IUPAC)

Nomenclature of Aldehydes

IUPAC

System

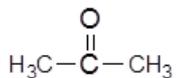
- o *Aromatic aldehydes* are usually designated as derivatives of the simplest aromatic aldehyde, *benzaldehyde*.



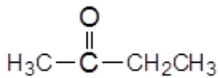
Nomenclature of Ketone

Common

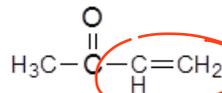
- o **Names** Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. **Alkyl ketone.**
- o In still other cases, traditional names are used.



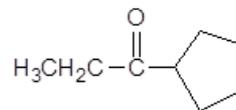
Acetone
(Dimethyl ketone)



Ethyl methyl ketone

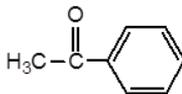


Methyl vinyl ketone

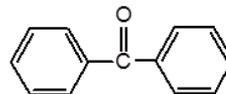


Cyclopentyl ethyl ketone

ر حسب الأجدية



Methyl phenyl ketone
(Acetophenone)



Diphenyl ketone
(Benzophenone)

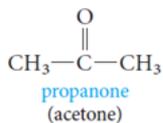
Nomenclature of Aldehydes

IUPAC

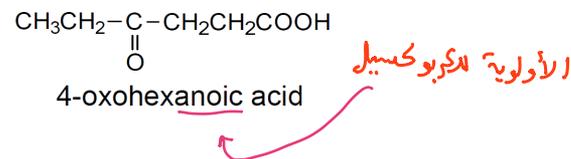
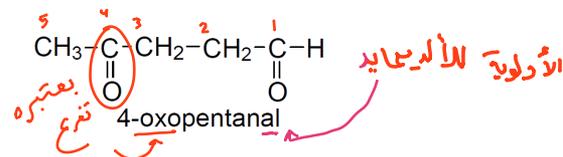
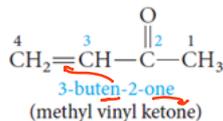
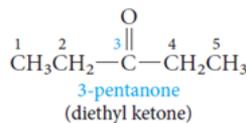
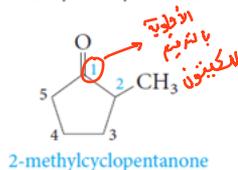
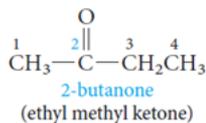
System

- o In the IUPAC system, **the ending for ketones is -one.**
- o The chain is numbered so that the **carbonyl carbon has the lowest possible number.**
- o For **cyclic ketones**, numbering always starts from the C=O group.
- o The prefix "**oxo**" is used when the ketone is not the principal functional group.

IUPAC
(Common)



cyclohexanone



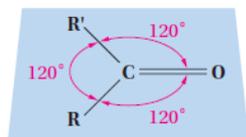
الأولوية للألدهيد مستحيلة
تكون جزء من الحلقة
لأنه ما سيكون عند
مجموعة الكربونيل قدرة
ترتبه بـ //

The Carbonyl

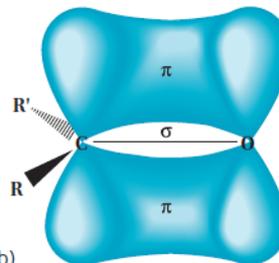
Group

o The structure and properties of the carbonyl group.

- The carbon–oxygen double bond consists of a sigma bond and a pi bond.
- The carbon atom is sp^2 -hybridized. The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120° .
- The pi bond is formed by overlap of a p orbital on carbon with an oxygen p orbital.
- There are also two unshared electron pairs on the oxygen atom. *in sp^2 orbitals*
- The C=O bond distance is 1.24Å, shorter than the C-O distance in alcohols and ethers (1.43Å).



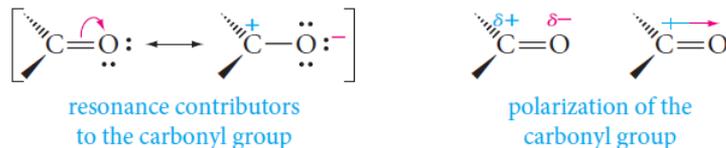
(a) *planner*



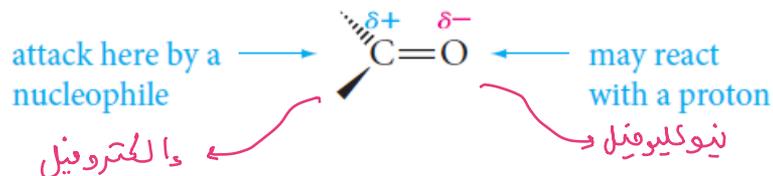
(b)

The Carbonyl Group

- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a highly **polarized bond**.



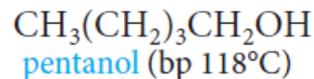
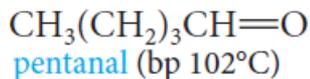
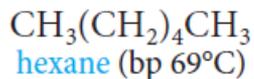
- As a consequence of this polarization, *most carbonyl reactions involve nucleophilic attack at the carbonyl carbon*, often accompanied by addition of a proton to the oxygen (electron rich).



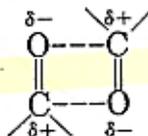
Physical Properties of Aldehydes and Ketones

Boiling

Points Carbonyl compounds boil at higher temperatures than hydrocarbons, but at lower temperatures than alcohols of comparable molecular weight.



➤ This is due to the intermolecular forces of attraction, called dipole-dipole interactions, which is stronger than van der Waals attractions but not as strong as hydrogen bonds.

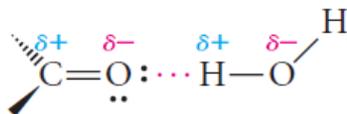


Dipole-dipole attractions among carbonyl compounds

Physical Properties of Aldehydes and Ketones

Solubility

- o Carbonyl compounds as aldehydes and ketones have a **C=O bond**, but **no O-H bond**, cannot form hydrogen bonds with themselves.
- o The **polarity of the carbonyl group** also affects the solubility properties of aldehydes and ketones.
- o Carbonyl compounds with **low molecular weights** are soluble in water as they can form hydrogen bonds with O-H or N-H compounds.



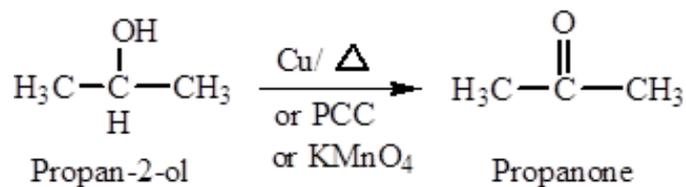
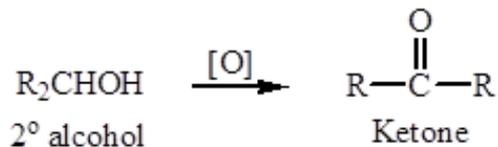
کملاں اور molecular weight
(عدد الكربونائین)

اقل کملاں ابھی اعجاز

Preparation of Aldehydes and Ketones

1) Oxidation of Primary and Secondary Alcohols

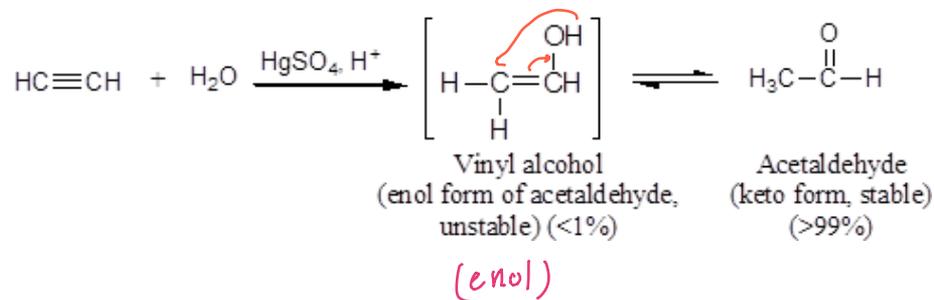
- o Oxidation of **secondary alcohols** yields **ketones**.



Preparation of Aldehydes and Ketones

2) Hydration of Alkynes *(addition reaction)*

- o Hydration of **acetylene** yields acetaldehyde (catalyzed by acid and mercuric).

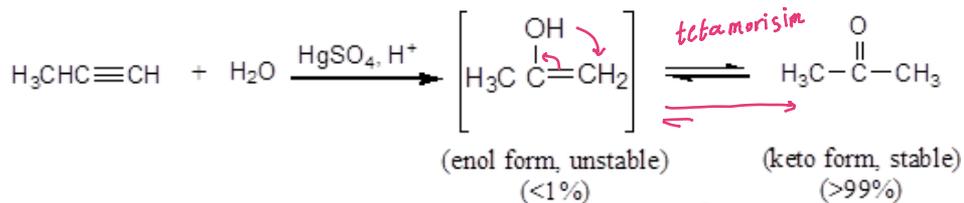
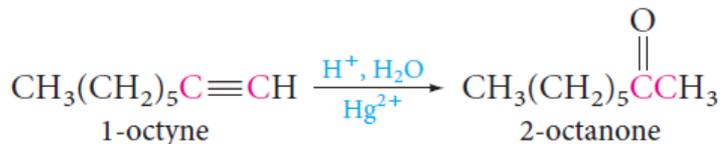


Preparation of Aldehydes and Ketones

2) Hydration of Alkynes

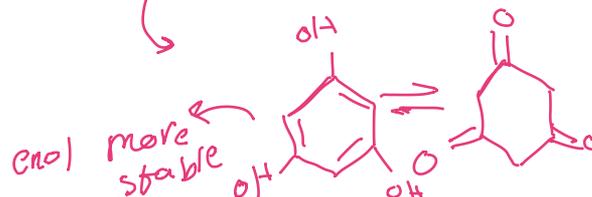
بعضي الدياتريد
↑

- Hydration of **terminal alkynes EXCEPT acetylene** yields ketones (catalyzed by acid and mercuric).



ملاحظة: صافية ر غير متلوبة

الكيتون دائما اكثر استقرارا من ال enol
إزا في حالة واحدة:



الفرق بين Terminal Alkyne و Internal Alkyne يكمن في موقع الرابطة الثلاثية في سلسلة الألكاين.

1. Terminal Alkyne (ألكاين طرفي):

• هو الألكاين الذي يحتوي على رابطة ثلاثية بين ذرتي كربون، بحيث تكون واحدة من هذه الذرات مرتبطة بذرة هيدروجين (في نهاية السلسلة).
• مثال: 1-بوتاين

2. Internal Alkyne (ألكاين داخلي):

• هو الألكاين الذي يحتوي على رابطة ثلاثية بين ذرتي كربون، وكل من ذرتي الكربون المرتبطتين بالرابطة الثلاثية تكونان مرتبطتين بسلاسل كربونية أخرى (أي أن الرابطة الثلاثية ليست في نهاية السلسلة).
• مثال: 2-بيوتاين

ليس

معلومة إضافية

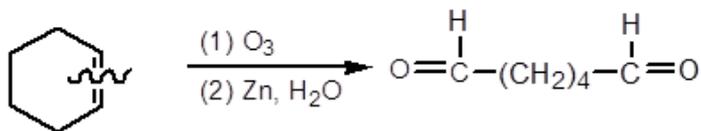
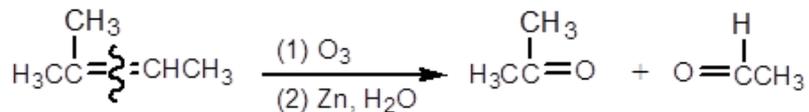
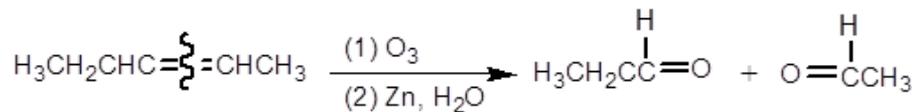
للتوضيح

غير مطلوب

Preparation of Aldehydes and Ketones

3) Ozonolysis of Alkenes

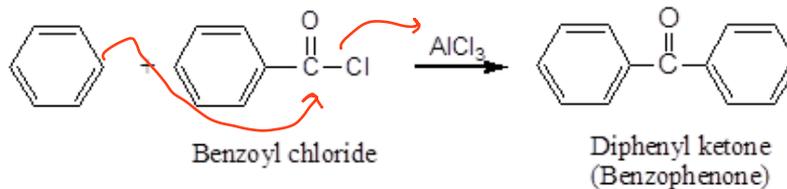
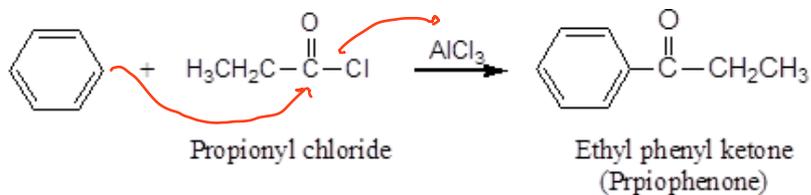
Product (aldehyde or ketone) depends on the **structure of alkene**.



Preparation of Aldehydes and Ketones

4) Friedel-Crafts Acylation

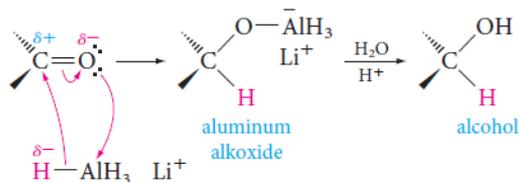
Preparing ketones that contain an aromatic ring.



Reactions of Aldehydes and Ketones

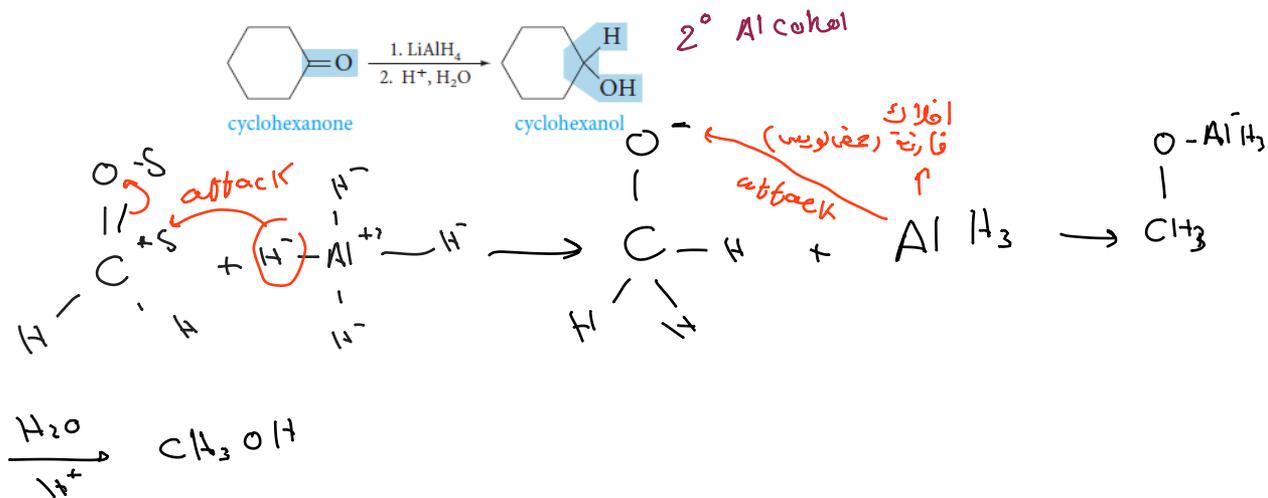
A) Reduction of Carbonyl Compounds

- Aldehydes and ketones are **easily reduced to primary and secondary alcohols**, respectively.
- The most common metal hydrides used to reduce carbonyl compounds are **lithium aluminum hydride (LiAlH₄)** and **sodium borohydride (NaBH₄)**.



النوكليوفيل في هذا
التفاعل هو H^- (Hydried)
في LiAlH_4

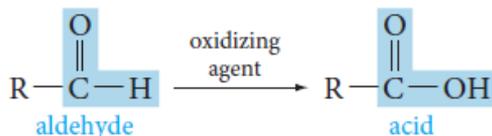
Example:



Reactions of Aldehydes and Ketones

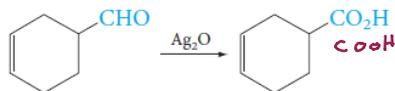
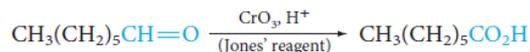
B) Oxidation of Carbonyl Compounds

- o Oxidation of aldehydes gives a carboxylic acid with the same number of carbon atoms.
- o Because the reaction occurs easily, many oxidizing agents, such as KMnO_4 , CrO_3 , Ag_2O and peracids (such as, perchloric acid HClO_4 , and permanganic acid HMnO_4). will work.



(الكيتون ما بيطي)
carboxylic acid

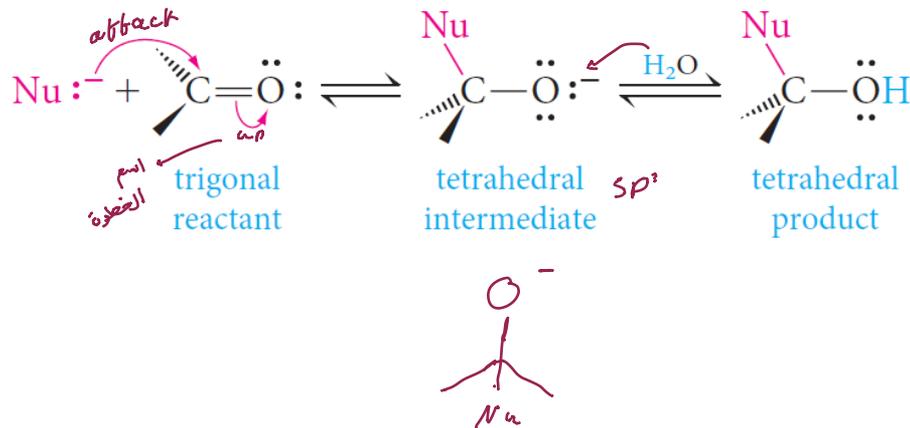
o Example:



Reactions of Aldehydes and Ketones

C) Nucleophilic Addition Reactions

- o Nucleophiles attack the carbon atom of a carbon-oxygen double bond because that **carbon has a partial positive charge**.
- o The overall reaction involves addition of a **nucleophile and a proton across the pi bond** of the carbonyl group (when carried out in alcohol or water).



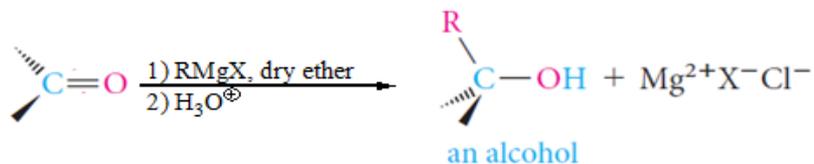
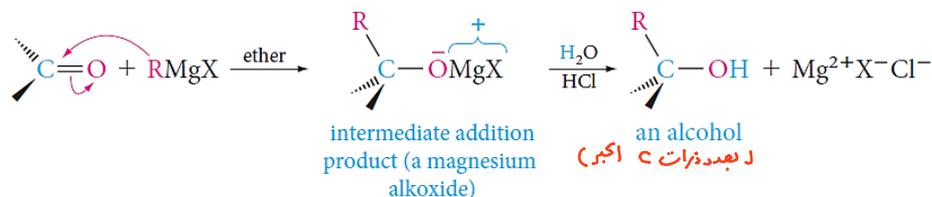
Reactions of Aldehydes and Ketones

C) Nucleophilic Addition

Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

- o *Grignard reagents act as carbon nucleophiles toward carbonyl compounds.*
- o The reaction of a Grignard reagent with a carbonyl compound provides a useful route to alcohols.



- o The type of carbonyl compound chosen determines the class of alcohol produced.

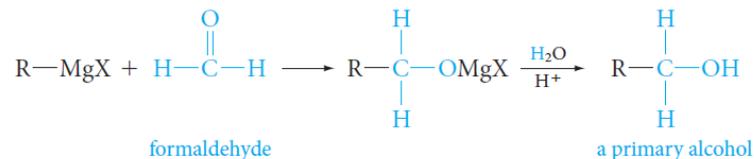
Reactions of Aldehydes and Ketones

C) Nucleophilic Addition

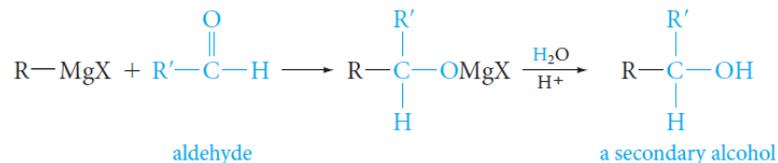
Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

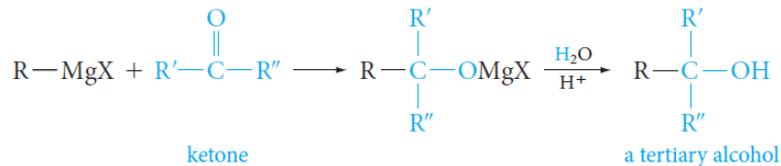
Formaldehyde gives primary alcohols.



o *Other aldehydes give secondary alcohols*



o *Ketones give tertiary alcohols.*



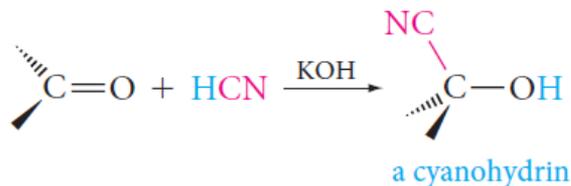
Reactions of Aldehydes and Ketones

C) Nucleophilic Addition

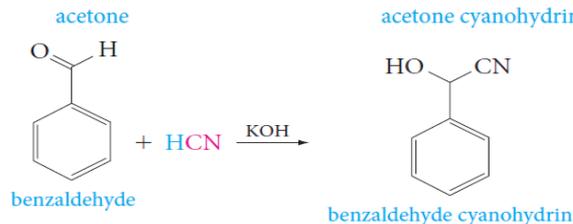
Reactions

2) Addition of Hydrogen Cyanide: Formation of

- o **Cyanohydrins** Hydrogen cyanide adds to the carbonyl group of aldehydes and ketones to form **cyanohydrins**, compounds with a hydroxyl and a cyano group attached to the same carbon.



o Example



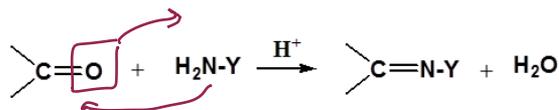
Reactions of Aldehydes and Ketones

C) Nucleophilic Addition

Reactions

3) Addition of Ammonia and Ammonia Derivatives

The addition of nitrogen nucleophile, such as ammonia(NH₃) and substituted ammonia (NH₂-Y).



لازم N على
الأقل عليها
هيدروجين

