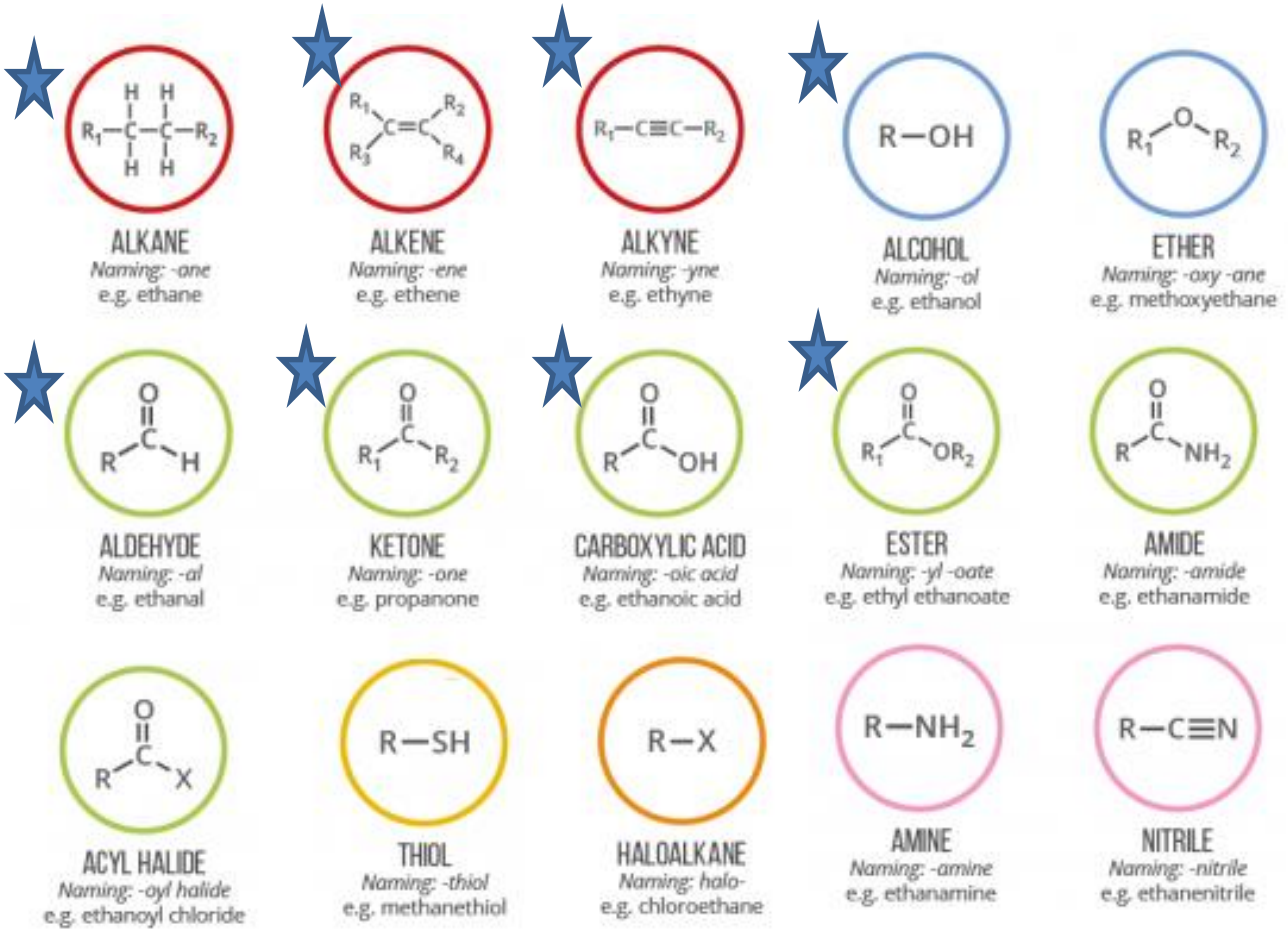
Chapter 4 (Continue)

Hydrocarbon Derivatives and their Reactions

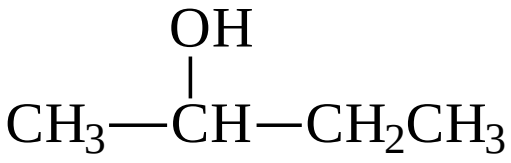
Function groups in organic compounds

Function group: It is a group of atoms in a molecule which is responsible for its chemical reactions and behavior.

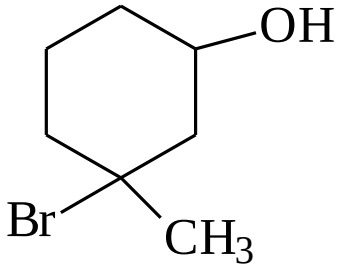


Alcohols: Preparation – properties - uses

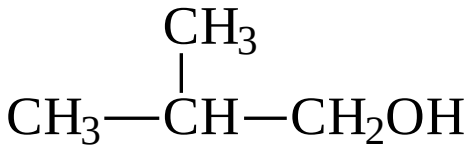
- **Alcohol**: organic compounds in which the hydroxyl functional group (–OH) is bonded to a saturated carbon atom.
- **Nomenclature**: add "ol" to the longest chain after removing "e" from alkane



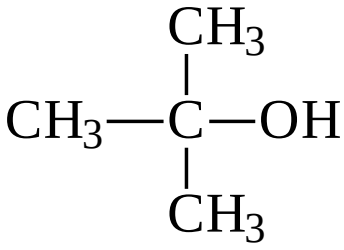
2-butanol or butyl alcohol



3-bromo-3-methylcyclohexanol



2-methyl-1-propanol
Or isobutyl alcohol

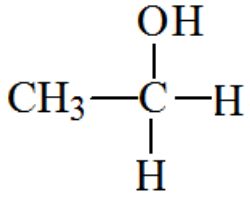


2-methyl-2-propanol

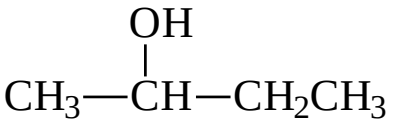
4-penten-2-ol

Classifications

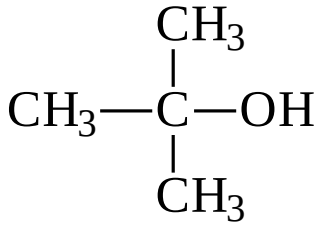
I) according to kind of the C-atom attached to OH:



1- Primary (1°): carbon with –OH bonded to one other carbon.



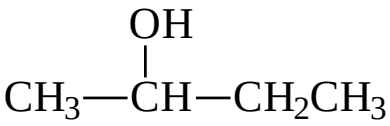
2- Secondary (2°): carbon with –OH bonded to two other carbons.



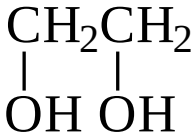
3- Tertiary (3°): carbon with –OH bonded to three other carbons.

II) according to numbers of OH:

1- Monohydric alcohol

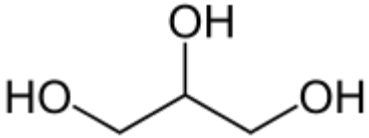


2- Dihydric alcohol



1,2-ethanediol (ethylene glycol)

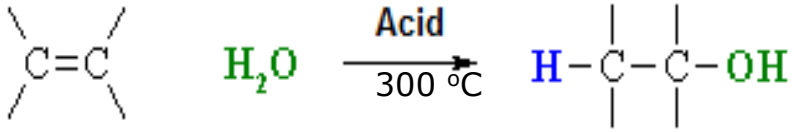
2- Trihydric alcohol



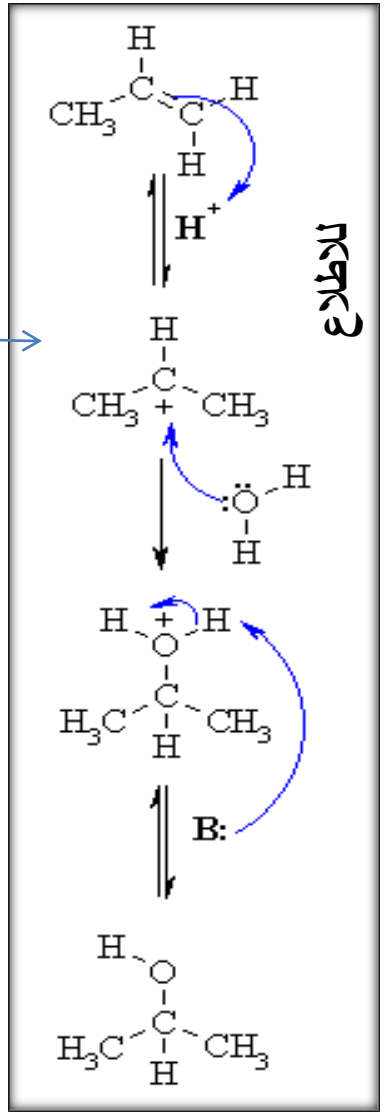
1,2,3-propanetriol (glycerol)

Preparation of alcohols

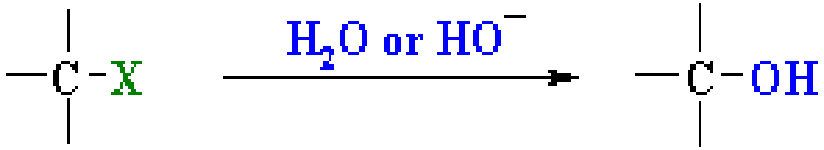
- Hydration of alkene:



Reaction mechanism



- Hydrolysis of alkyl halides

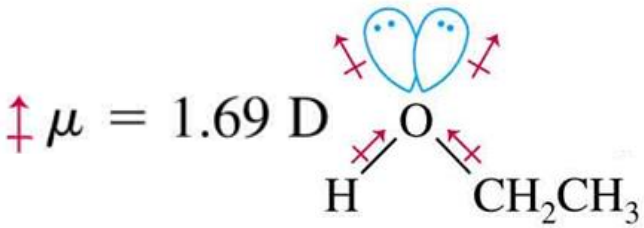


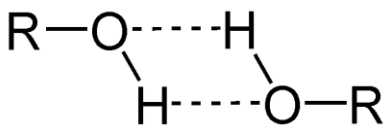
- in industry: preparation of methanol from hydrogenation of Carbon monoxide CO

$$CO + 2H_2 \longrightarrow CH_3OH$$

Physical properties

- Alcohols are Polar compounds, they are the third in terms of **polarity.**
- They have high boiling points due to hydrogen bonding between molecules. B.p of 1° alcohol > 2° > 3°
- Small alcohols are miscible in water, but solubility decreases as the size of the alkyl group increases. Solubility of 1° alcohol > 2° > 3°





H-bonding

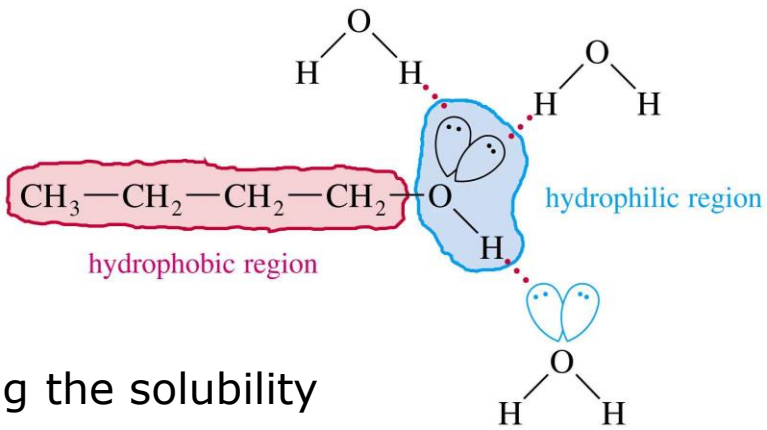


Figure describing the solubility

TABLE 10-2 Water Solubility of Alcohols (at 25°C)

Alcohol	*Solubility in Water*
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible

Uses of alcohols

As a fuel

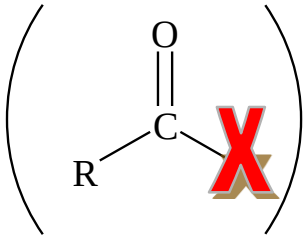
- Methanol and ethanol burns to give CO_2 and water.
- They can be used as a fuel alone, or in mixtures with petrol (gasoline). "Gasohol" is a petrol / ethanol mixture containing about 10 - 20% ethanol.
- Some countries can produced ethanol by fermentation to replace the fossil fuel (to reduce imports of petrol).

- **As a solvent**
- Ethanol and methanol are widely used as a solvent.
- Ethanol is relatively safe than methanol, and can be used to dissolve many organic compounds which are insoluble in water.
- They are used in manufacturing many perfumes and cosmetics.

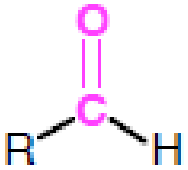
Hydrocarbon derivatives (carbonyl compounds)

Their preparation – properties – reactions –uses

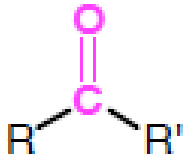
Hydrocarbon derivatives containing carbonyl groups



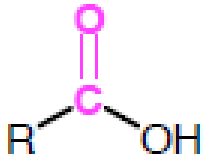
Carbonyl group



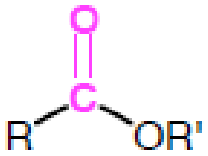
Aldehyde
RCHO



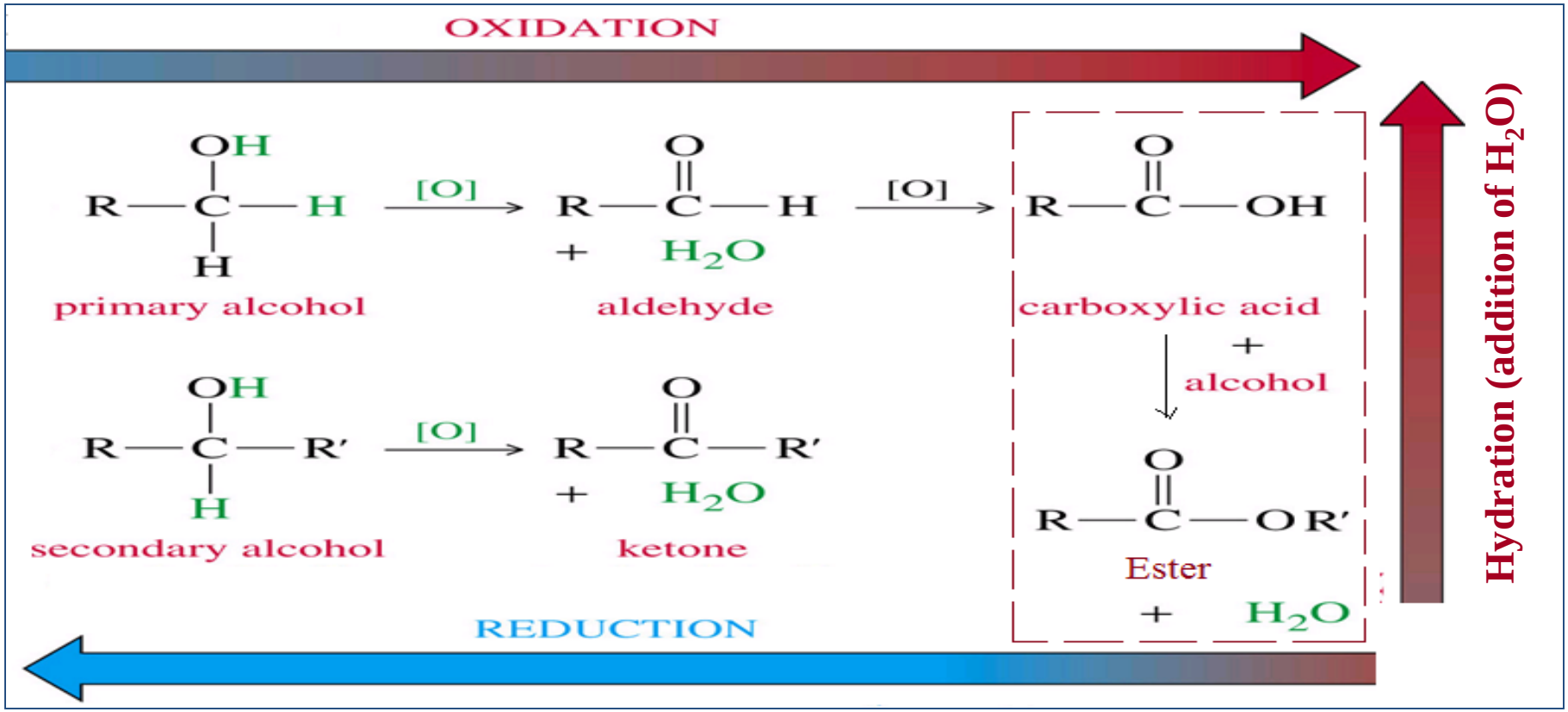
Ketones
RCOR'



Carboxylic acids
RCOOH

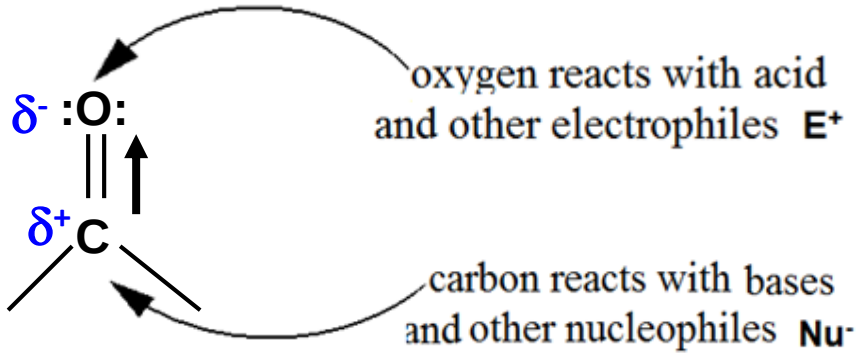


Esters
RCOOR'



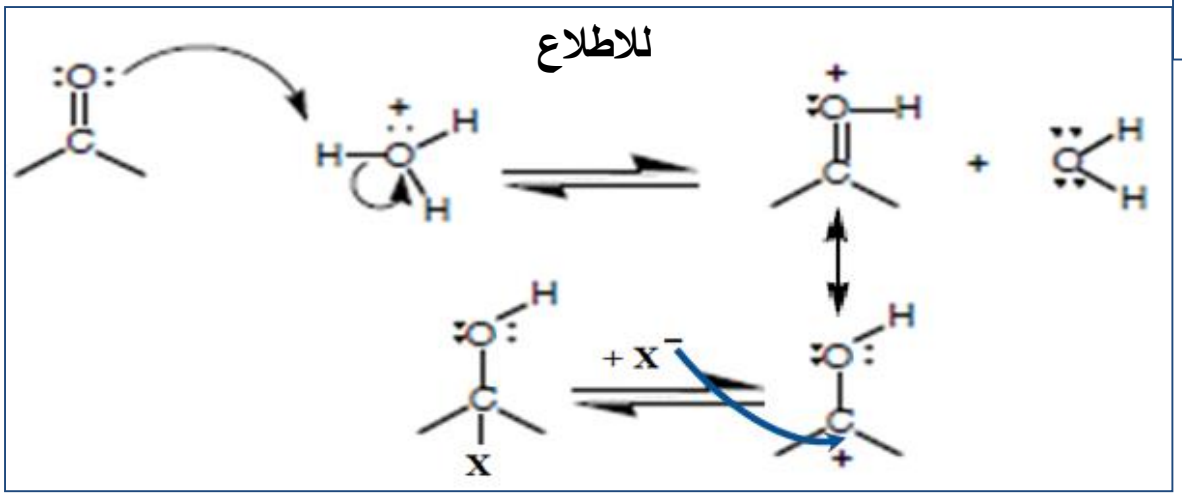
Reactions occur in carbonyl group >C=O

C=O bond of the carbonyl group is polarized. This polarization is responsible for the characteristic reactions of carbonyl compounds.



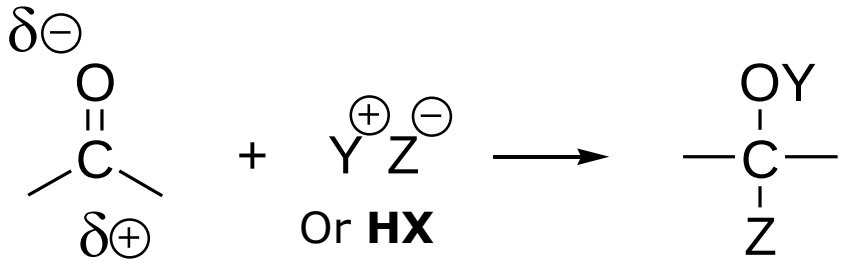
Ex. Reaction of carbonyl compound with an acid :

$$HX + H_2O \longrightarrow \underset{E^+}{H_3{}^+O} + \underset{Nu^-}{X^-}$$



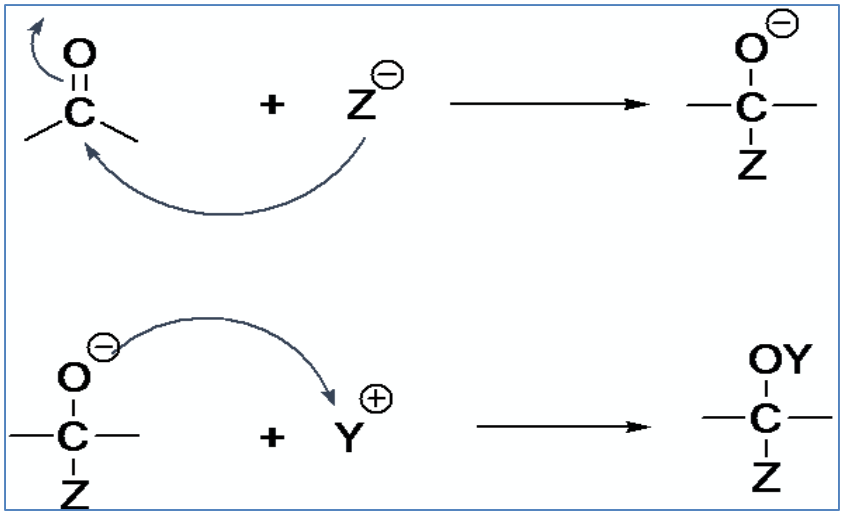
General Reactions in carbonyl compounds

1- Nucleophilic Addition Reactions

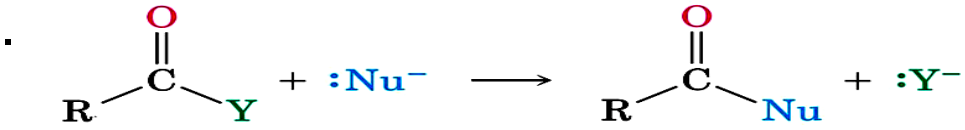


Occur in aldehyde and ketones

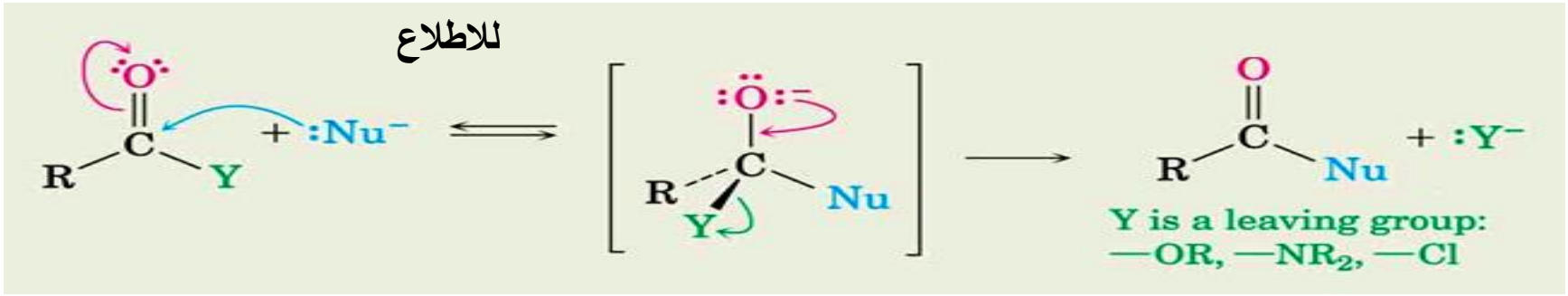
Mechanism



2- Nucleophilic Substitution Reactions:



These type of reactions occur in carboxylic acids and esters.



Aldehydes & ketones

- They are carbonyl compounds that contain C=O group.

They are similar in most properties such as:

1) They are polar molecules, so they have higher boiling points than alkenes of similar molecular weight but have lower boiling points than alcohols of similar molecular weight.
2) They undergo nucleophilic addition reactions.

- But because aldehydes contain H atom attached to the C=O, there are some differences between them such as:

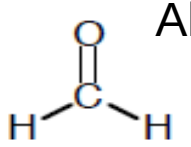
1) Aldehydes are quiet easily oxidized, but ketones are oxidized with difficultly.
2) Aldehydes are more reactive than ketones toward nucleophilic addition.

Aldehydes & ketones

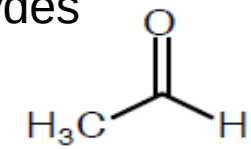
➢**Nomenclature:**

- In aldehydes: replace the (e) in alkane by (al), but in ketones, replace it by (one)

Aldehydes

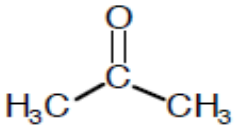


Methanal
(formaldehyde)

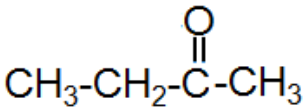


Ethanal
(acetaldhyde)

Ketones



Propanone
(acetone)



2-butanone

➢**preparation:**

1- From oxidation of alcohols:

primary alcohol gives aldehyde, secondary alcohol gives ketones:

$$RCH_2OH \xrightarrow{[O]\ \text{(pyridinium chlorocromate)}} RCHO$$

$$R_2CHOH \xrightarrow{[O]\ \text{chromic acid}} R_2C{=}O$$

2- From reduction of carboxylic acid:

$$RCOOH \xrightarrow{LiAlH_4} RCHO$$

Chemical Reactions of aldehydes & ketones

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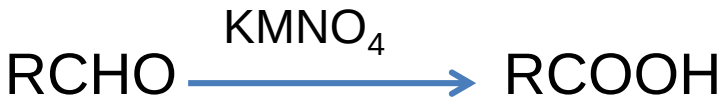
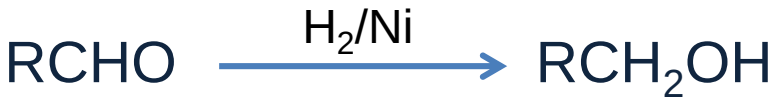
➢ **Oxidation:**, aldehydes are oxidized to carboxylic acids by mild oxidizing agents, but ketones are not:



- **Reduction:**, by reducing agents,

❖ Aldehydes are reduced to primary alcohols:



❖ Ketones are reduced to secondary alcohols:

Uses of Aldehydes and Ketones:

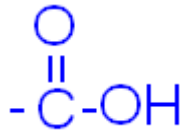
➢Uses of Aldehydes:

- Around 6 millions tons of formaldehyde produces every year. It is mostly used in the formation of resins, when mixed with melamine, urea, etc.
- 2.5 millions tons butyraldehyde are produce every year. It is mainly used as a plasticizer.
- Some other aldehydes are used as ingredients in flavors and deodorants.

➢ Uses of Ketone:

- Acetone, and cyclohexanone, are the most important ketones.
- Ketones are produced at very high scale to be used in medicine ,solvents, or in polymers synthesis.

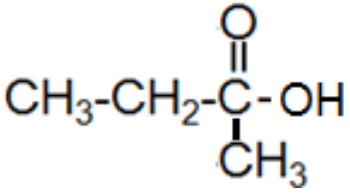
II) Carboxylic Acids

- Organic compounds having one or more carboxylic groups. 
- This group is composed of two functional groups:

  carbonyl group -C=O , and the hydroxyl group -OH
- They are not strong acids as inorganic acids (HCl, HNO_3…)
- Their acid strength increases as the # of (COOH) increases.
- Their IUPAC name is by replacing the letter (e) in the equivalent alkane, by the suffix (oic):

* HCOOH = methanoic acid (formic or ants acid),

** CH_3COOH = ethanoic acid (vinegar or acetic acid).

***  = 2- butanoic acid

Preparation of Carboxylic Acids

1- Oxidation of primary alcohol:

$$CH_3CH_2OH \xrightarrow{[O]/\ K_2Cr_2O_7} CH_3CHO \xrightarrow{[O]} CH_3COOH + H_2O$$

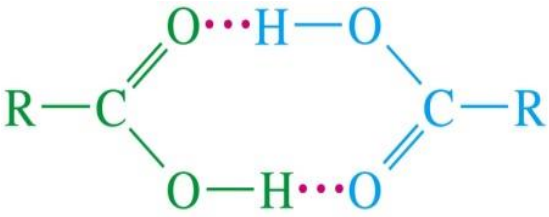
2- Hydrolysis of nitriles:

$$RC{\equiv}N + H_2O \xrightarrow{H^+/\Delta} RCOOH + NH_3$$

Their physical properties:

1- First members are liquids, mild members are oily, and the highest members are solid.

2- Their solubility in water decreases with the length of the carbon chain.



hydrogen-bonded acid dimer

3- They have higher boiling points than similar alcohols, due to dimer formation.

Uses of Carboxylic Acid

❖ Most of carboxylic acids are produced on a large scale for industrial purpose.

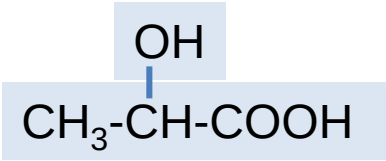
❖ In industry, carboxylic acids are used as additives or solvents in food production, drugs, and polymers, and some also used as a food preservative, chelating agent.

❖Formic acid is used in manufacturing of dyes, insecticides, drug and plastic.

❖Acetic acid is used in home as vinegar (4%), synthetic silk, dyes, and food additives.

❖Lactic acid (found in milk) generated in human body as a result of hard effort, and causes a construction of muscles.

❖Salysilic acid is used in the manufacture of Cosmetics and aspirin



Lactic acid

III) Organic Esters

➢ Organic compound produced from reacting carboxylic acids with alcohols in presence of conc H_2SO_4 :

$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(Ethanoic acid) (Ethyl alcohol) (ethylethanoate ester)

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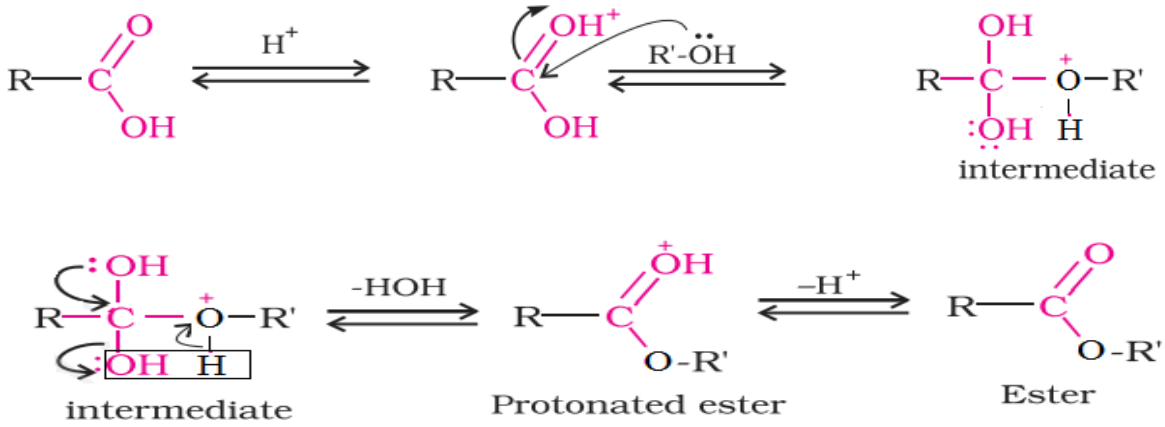
The reaction mechanism of the ester formation is:



➢ Their names are derived from the name of acid and alkyl group of alcohol:

* $HCOOCH_3$ = **methyl** methanoate ester,

** $CH_3COOC_2H_5$ = **ethyl**ethanoate ester

Properties of Organic Esters

Their physical properties:

1) Their B.P is lower than that of carboxylic acids or alcohol due to the absence of H-bonding.

2- Their odor is pleasant, so they are used in preparation of perfumes & flavors.

3- They also used in producing polyesters, dacron, and drugs such as Asprin.

Their chemical properties:

1- Acid hydrolysis:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

2- Base hydrolysis (saponification):

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$