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لطلبة الصف الثاني

Carbonyl Compounds

In the 2nd. Semester the following topics will considered:

1- Carbonyl Compounds (Aldehydes & Ketones).
2- Carboxylic Acids.
3- Functional Derivatives of Carboxylic Acids.
4- Carbanion I and II.
5- Amines.
6- Phenols

Carbonyl Compounds

Are compounds that contain C=O group

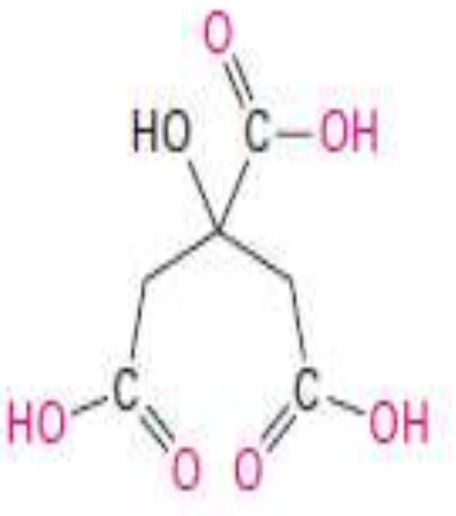
-These compounds occur everywhere.

-Most **biological molecules** contain carbonyl groups

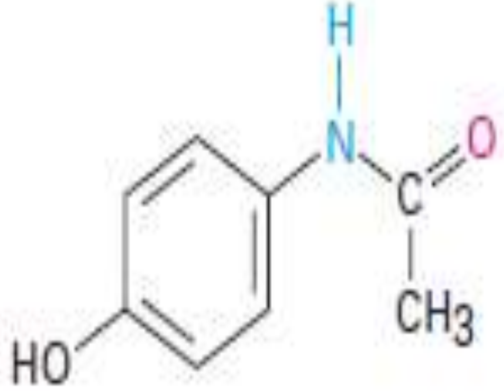
- most **pharmaceuticals**

- and many of **the synthetic chemicals** that touch our everyday lives

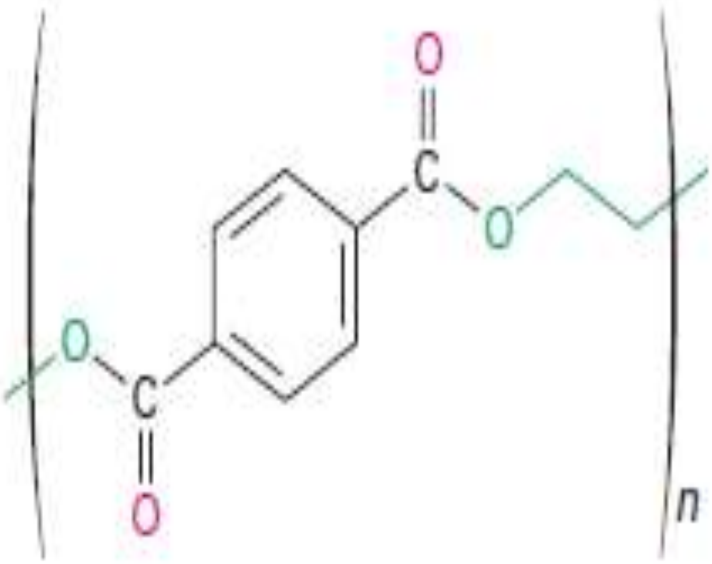
- **Citric acid** found in lemons and oranges.
- **Acetaminophen** the active ingredient of many over shelf medicine and
- **Dacron** is a synthetic polyester



Citric acid
(a carboxylic acid)



Acetaminophen
(an amide)

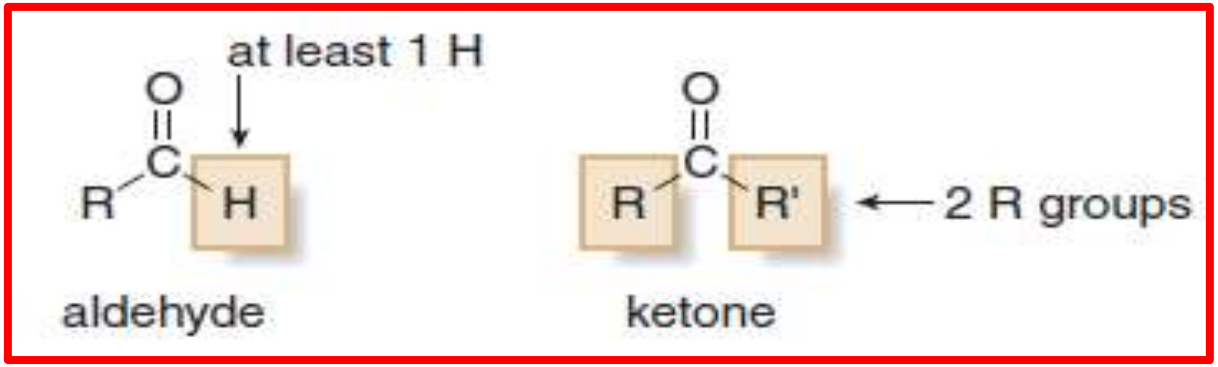


Dacron
(a polyester)

Kinds of carbonyl compounds

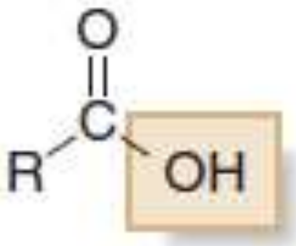
★ Two broad classes of compounds contain a *carbonyl group:*

[1] Compounds that have only carbon and hydrogen atoms bonded to the carbonyl group

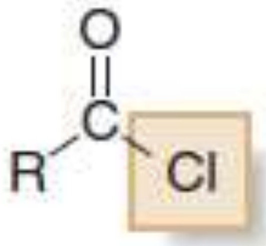


- ⇒ An **aldehyde** has at least one H atom bonded to the carbonyl group.
- ⇒ A **ketone** has two alkyl or aryl groups bonded to the carbonyl group.

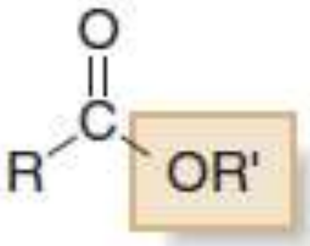
[2] Compounds that contain an electronegative atom bonded to the carbonyl group



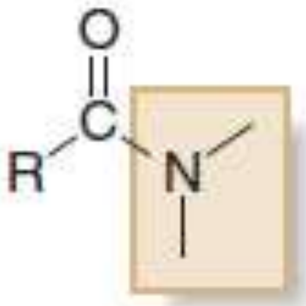
carboxylic acid



acid chloride



ester

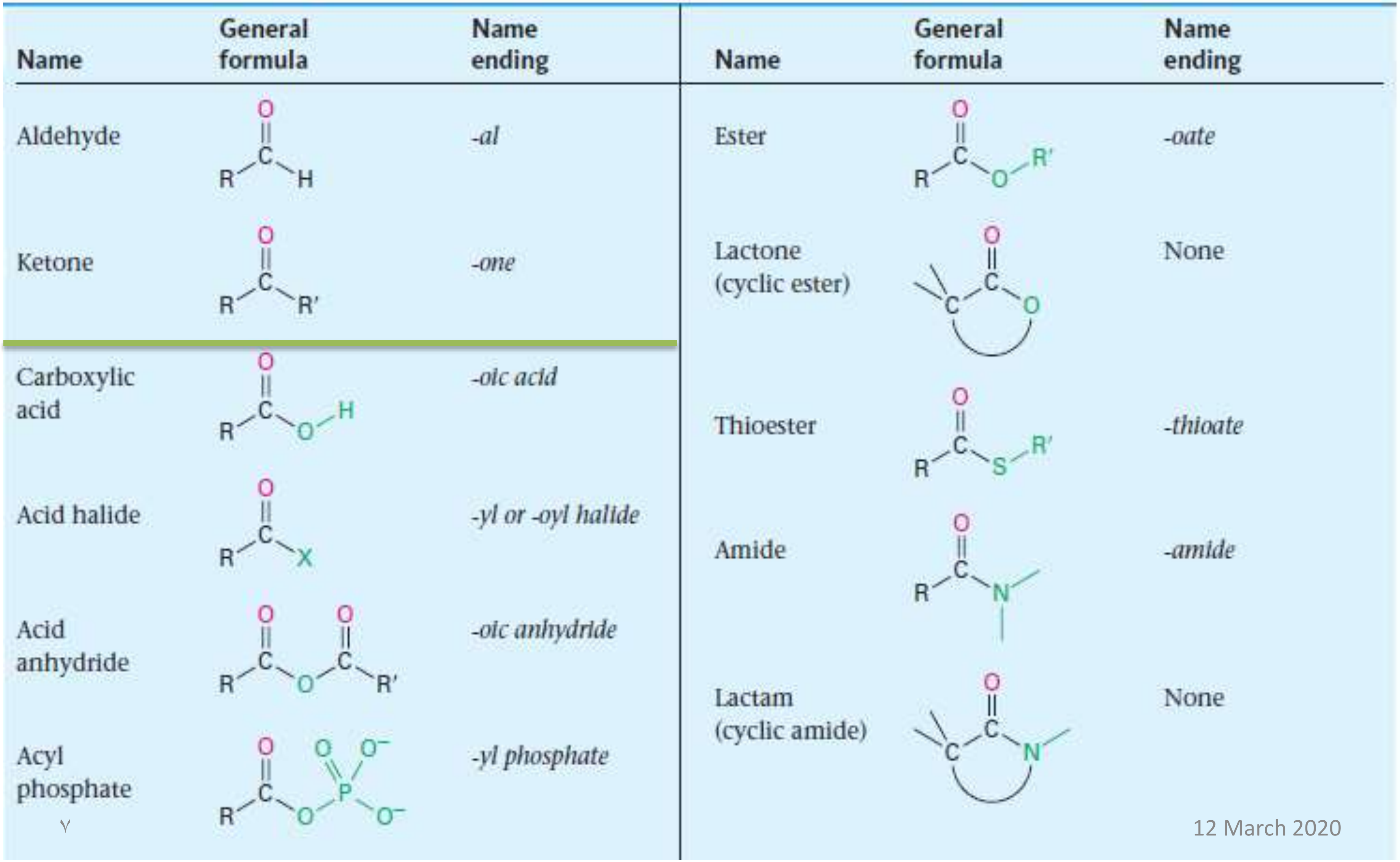


amide

➡ Each of these compounds contains an electronegative atom (Cl, O, or N) capable of acting as a **leaving group.**

➡ Acid chlorides, esters, and amides are often called carboxylic acid derivatives, because they can be synthesized from carboxylic acids

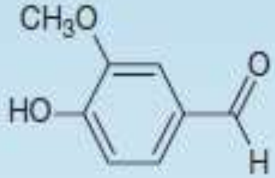
The table below shows some of the many different kinds of carbonyl compounds



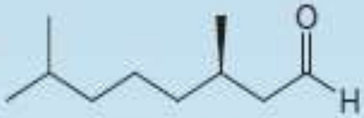
Name	General formula	Name ending
Aldehyde		*-al*
Ketone		*-one*
Carboxylic acid		*-oic acid*
Acid halide		*-yl or -oyl halide*
Acid anhydride		*-oic anhydride*
Acyl phosphate		*-yl phosphate*
Ester		*-oate*
Lactone (cyclic ester)		None
Thioester		*-thioate*
Amide		*-amide*
Lactam (cyclic amide)		None

ALDEHYDES and KETONES

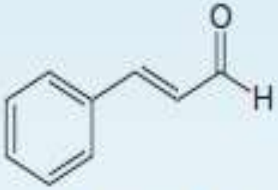
Figure 21.6 Some naturally occurring aldehydes with strong odors



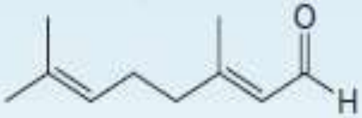
vanillin
(flavoring agent from
vanilla beans)



citronellal
(lemony odor, isolated
from lemon grass)



cinnamaldehyde
(odor of cinnamon)



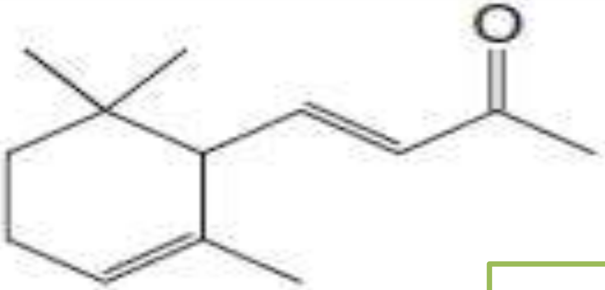
geranial
(lemony odor, isolated
from lemon grass)

cucumber aldehyde

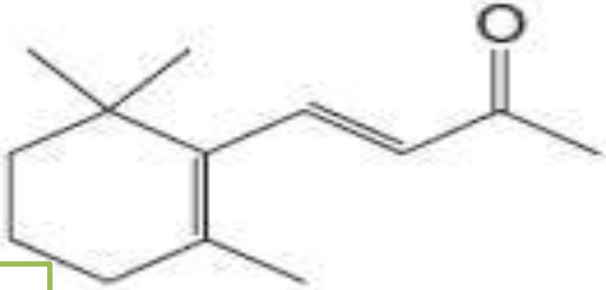
odor of a freshly cut cucumber

Some Naturally occurring Ketones

Used in Perfumes Formulation:



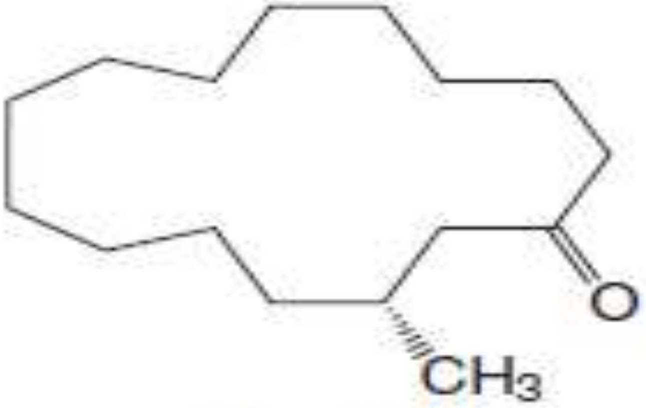
α-Ionone



β-Ionone

From roses oils

Two ketones from exotic natural sources are muscone (from the Himalayan musk deer) and civetone (from the African civet cat).

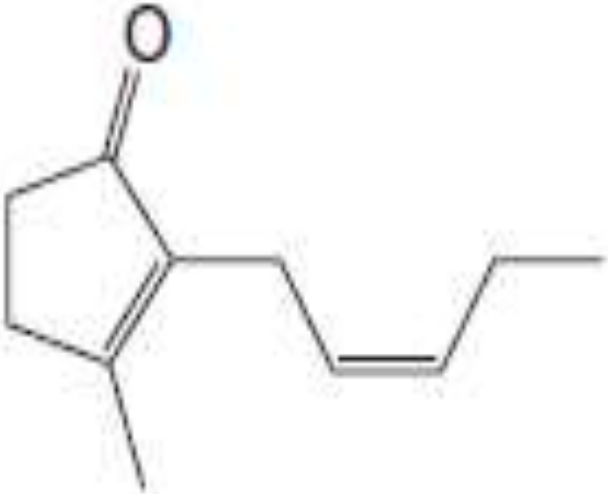


Muscone

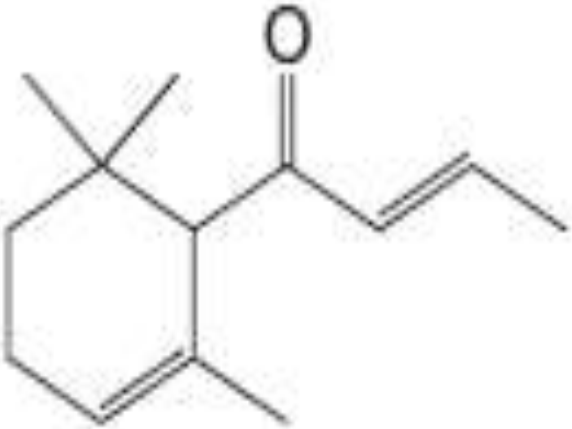
Civetone

(Z)-Jasmone (with the odor of jasmine) and α-damascone (odor of roses)

All of these ketones can be obtained from natural sources.



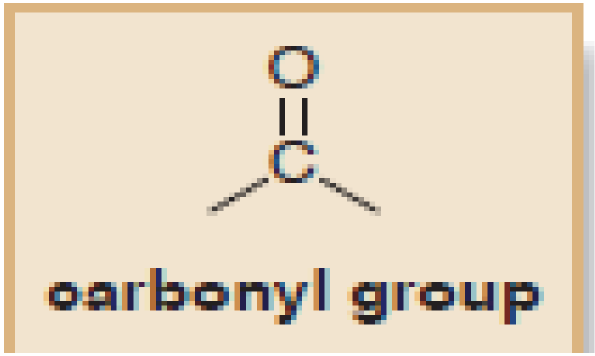
Z-Jasmone



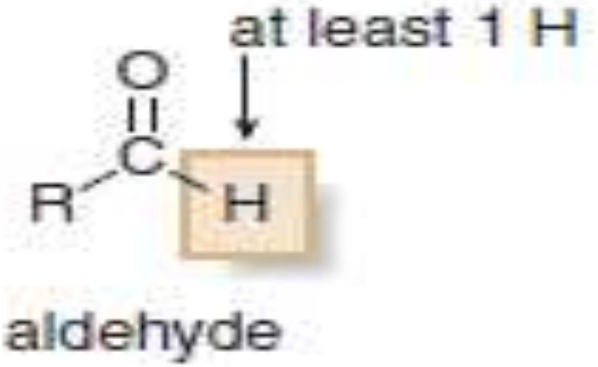
α-Damascone

Structure: The **similarity** between ald. & ketones:

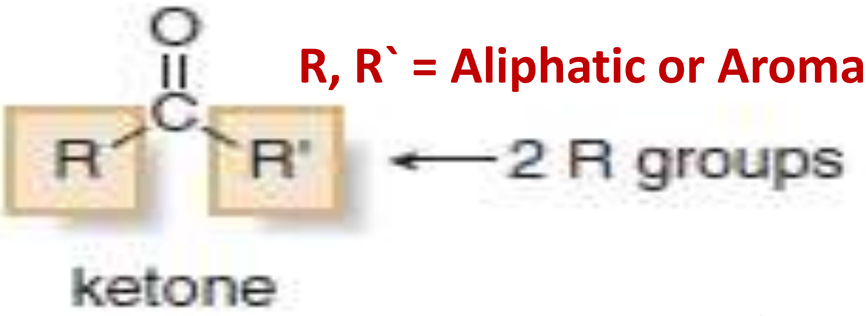
Both aldehydes and ketones contain carbonyl group



- An aldehyde has at least one H atom bonded to the carbonyl group.
- A ketone has two alkyl or aryl groups bonded to the carbonyl group.



R, R` = Aliphatic or Aromatic

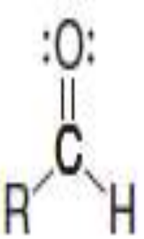


The **difference** between **aldehydes. & ketones:**

- **Aldehydes** are **more reactive** than **ketones** towards Nucleophilic attack, for both **Steric** and **Electronic** reasons

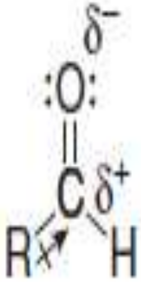
- The two R groups bonded to the ketone carbonyl group make it more crowded, so nucleophilic attack is more difficult.
- The two electron-donor R groups stabilize the partial charge on the carbonyl carbon of a ketone, making it more stable and less reactive.

Aldehydes—more reactive



Less steric hindrance with only one R group

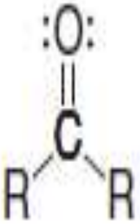
less crowded



Only one R stabilizes the positive charge.

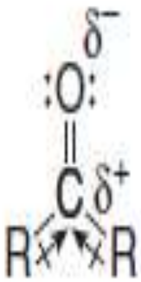
less stable

Ketones—less reactive



Two R's increase steric hindrance.

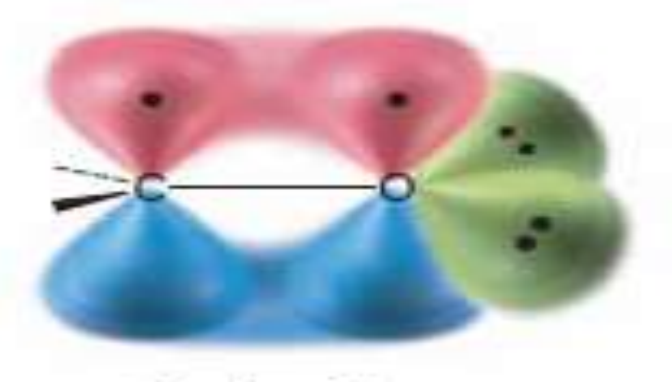
more crowded



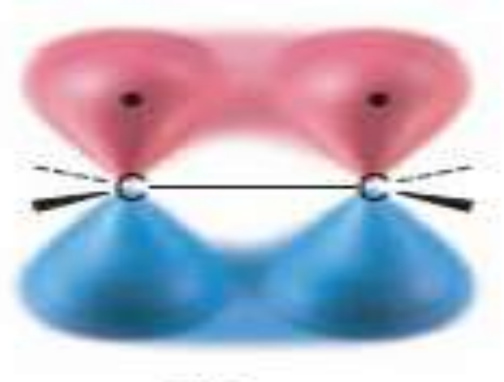
Two R's stabilize the positive charge.

more stable

Nature of the carbonyl group

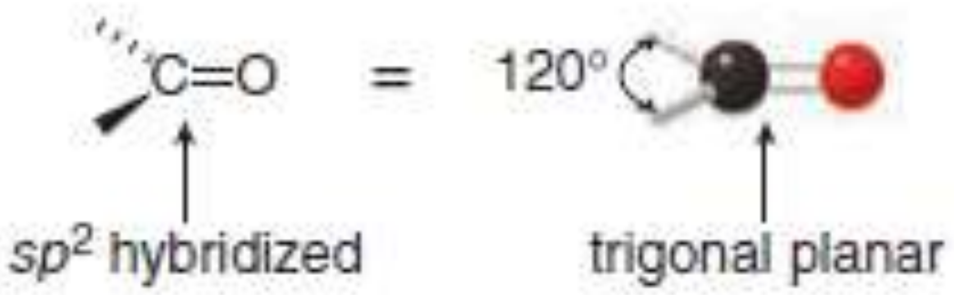


Carbonyl group

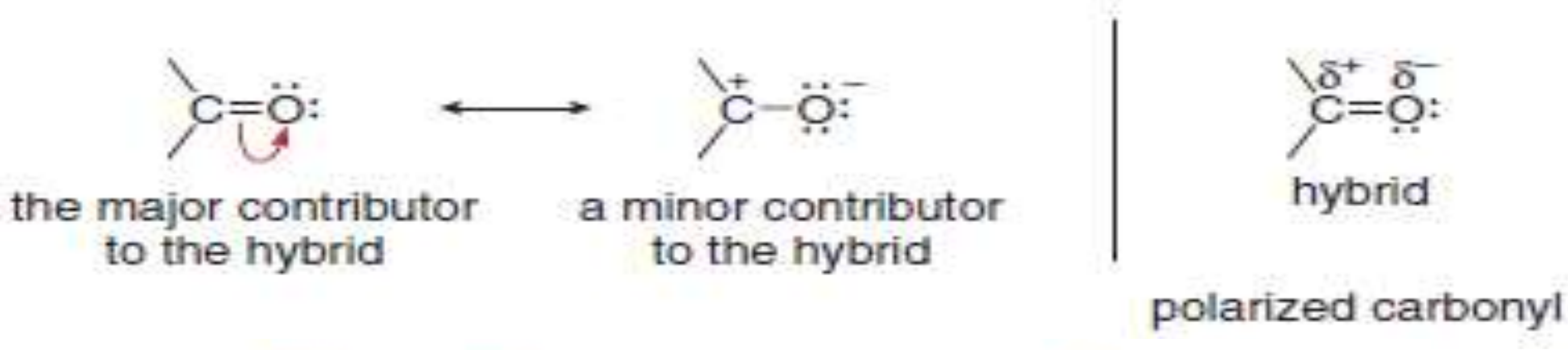


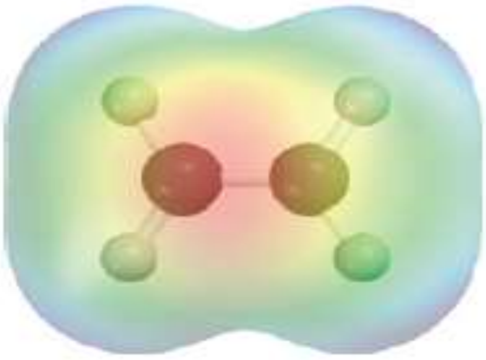
Alkene

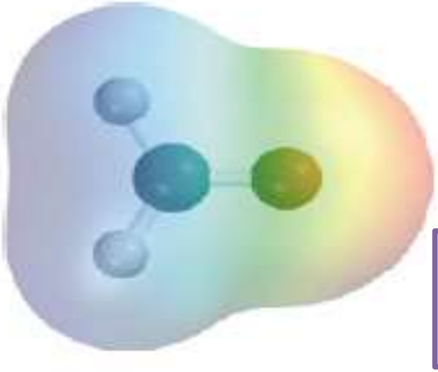
- Carbon bonded to 3 atoms
- Sp2 Hybridized
-Trigonal planner
-Bond Angle 120



- In one important way the C=O & C=C double bonds are **very different.**
- The presence of the **high electronegative oxygen** make carbonyl more polar.




(*a*) Ethylene


(*b*) Formaldehyde

Electrostatic Potential Map

Nomenclature of Aldehydes

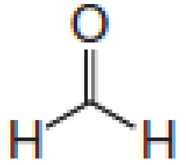
1- According to the IUPAC name:

IUPAC (International Union of Pure and Applied Chemistry)

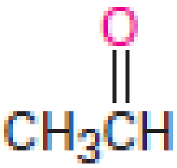
1- Select the longest chain carrying the –CHO group & give the name of the corresponding alkane.

2- Change the suffix –e of the parent alkane to –al

3- Number the chain so that the –CHO group takes no. 1

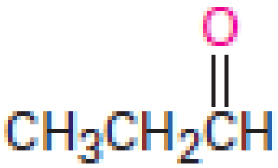


Methanal



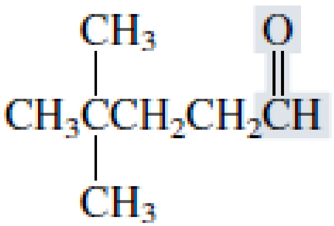
$CH_3\overset{\overset{O}{\|}}{C}H$

Ethanal



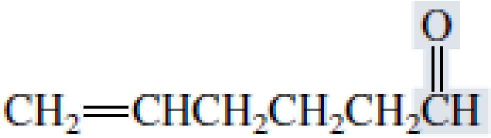
$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

Propanal



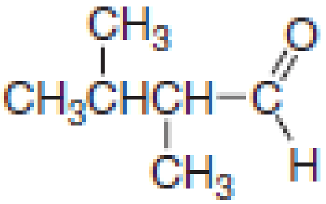
$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}H$

4,4-Dimethylpentanal

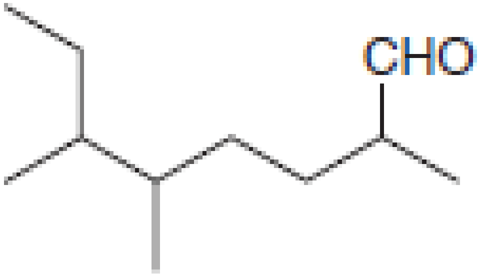


$CH_2{=}CHCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$

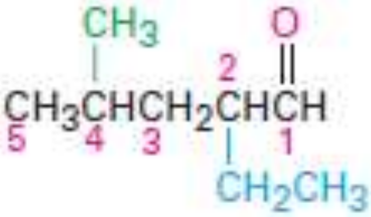
5-Hexenal



2,3-dimethylbutanal

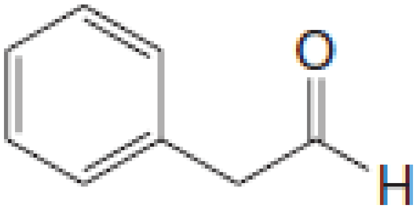


5-Chloropentanal

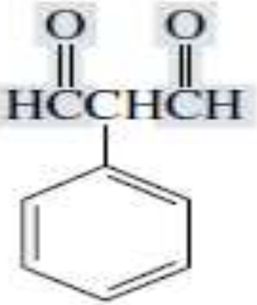


$CH_3\overset{CH_3}{C}HCH_2\underset{CH_2CH_3}{C}H\overset{O}{\overset{\|}{C}}H$

2-Ethyl-4-methylpentanal

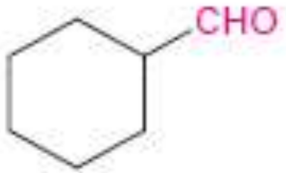


Phenylethanal

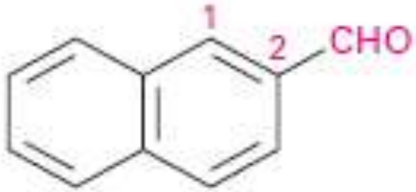


2-Phenylpropanedial

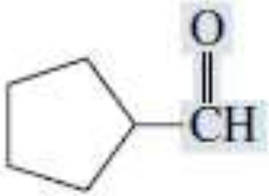
- For cyclic aldehydes in which the –CHO group is directly attached to a ring, the suffix *-carbaldehyde* is used.



Cyclohexanecarbaldehyde



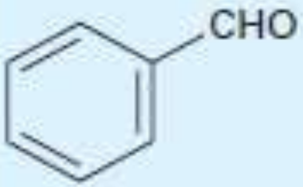
2-Naphthalenecarbaldehyde



Cyclopentanecarbaldehyde

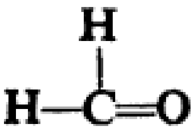
- A few simple and well-known aldehydes have common names that are recognized by IUPAC. Several that you might encounter are listed in Table 19.1.

Table 19.1 Common Names of Some Simple Aldehydes

Formula	Common name	Systematic name
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$H_2C{=}CHCHO$	Acrolein	Propenal
$CH_3CH{=}CHCHO$	Crotonaldehyde	2-Butenal
	Benzaldehyde	Benzenecarbaldehyde

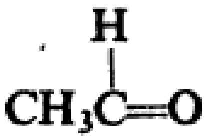
Common Names for Aldehydes

The common names of aldehydes are derived from the names of the corresponding carboxylic acids by replacing *-ic acid* by *-aldehyde*.



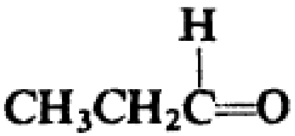
$\mathrm{H{-}\overset{H}{\overset{|}{C}}{=}O}$

Formaldehyde
Methanal



$\mathrm{CH_3\overset{H}{\overset{|}{C}}{=}O}$

Acetaldehyde
Ethanal



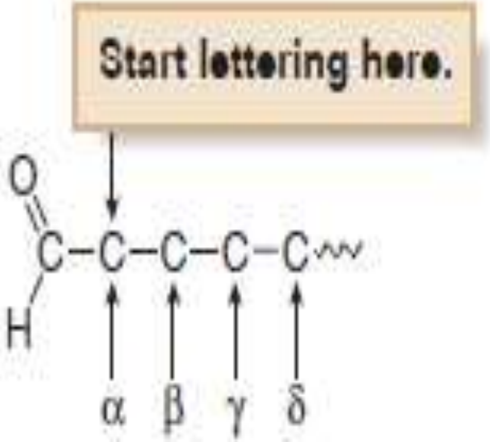
$\mathrm{CH_3CH_2\overset{H}{\overset{|}{C}}{=}O}$

Propionaldehyde
Propanal

$\mathrm{CH_3CH_2CH_2\overset{H}{\overset{|}{C}}{=}O}$

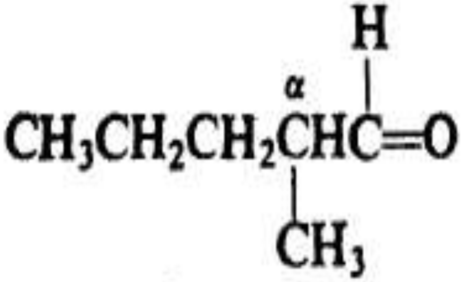
***n*-Butyraldehyde**
Butanal

Greek letters are used to designate the location of substituents in common names. The carbon adjacent to the CHO group is the α carbon, and so forth down the chain.



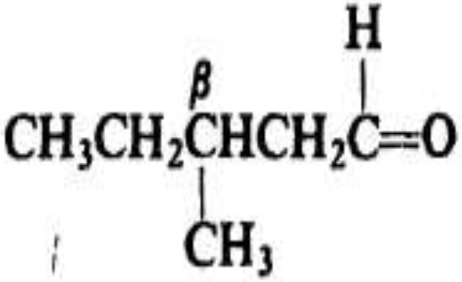
Start lettering here.

Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to *alpha* of the common name.



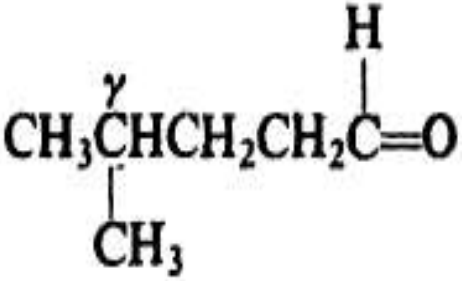
$CH_3CH_2CH_2\underset{CH_3}{\overset{\alpha}{C}}H\overset{H}{C}{=}O$

α-Methylvaleraldehyde
2-Methylpentanal



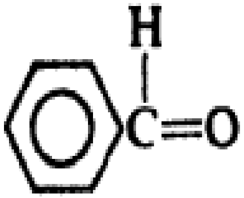
$CH_3CH_2\underset{CH_3}{\overset{\beta}{C}}HCH_2\overset{H}{C}{=}O$

β-Methylvaleraldehyde
3-Methylpentanal

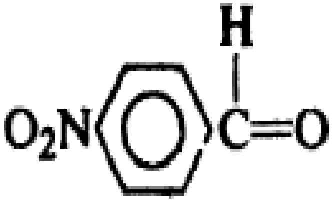


$CH_3\underset{CH_3}{\overset{\gamma}{C}}HCH_2CH_2\overset{H}{C}{=}O$

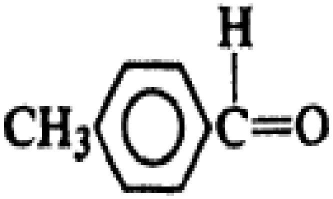
Isocaproaldehyde
γ-Methylvaleraldehyde
4-Methylpentanal



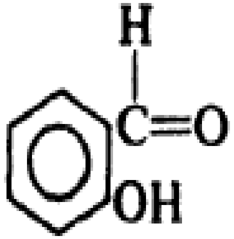
Benzaldehyde



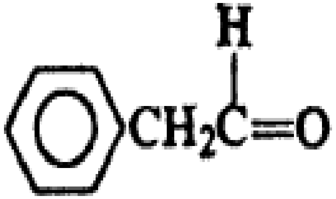
p-Nitrobenzaldehyde



p-Tolualdehyde

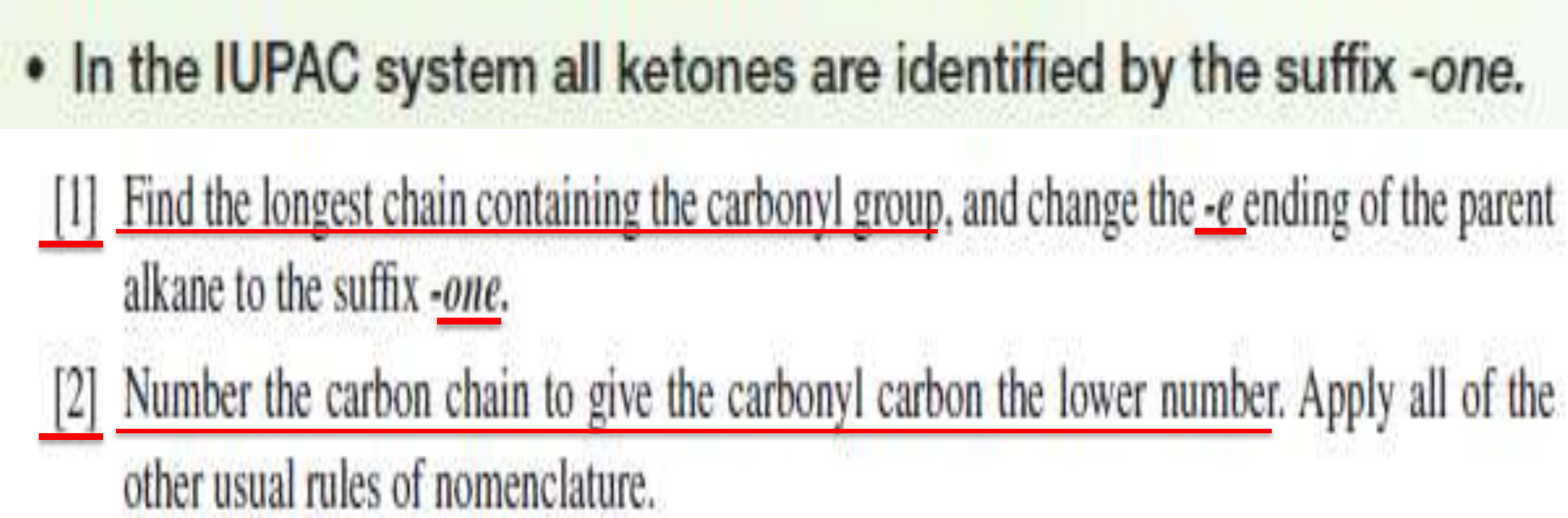


Salicylaldehyde
(*o*-Hydroxybenzaldehyde)



Phenylacetaldehyde
(Phenylethanal)

Nomenclature of ketones

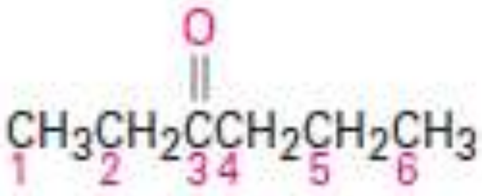


- In the IUPAC system all ketones are identified by the suffix *-one*.

[1] Find the longest chain containing the carbonyl group, and change the *-e* ending of the parent alkane to the suffix *-one*.

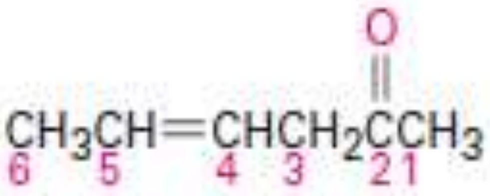
[2] Number the carbon chain to give the carbonyl carbon the lower number. Apply all of the other usual rules of nomenclature.

notice the new rules for nomenclature



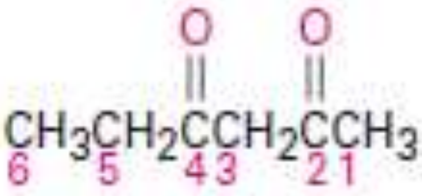
$CH_3CH_2C(=O)CH_2CH_2CH_3$

3-Hexanone
(New: Hexan-3-one)



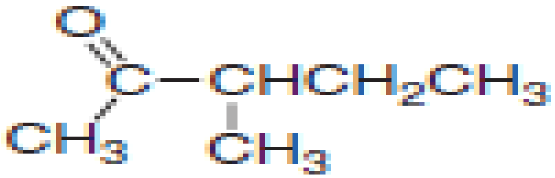
$CH_3CH{=}CHCH_2C(=O)CH_3$

4-Hexen-2-one
(New: Hex-4-en-2-one)



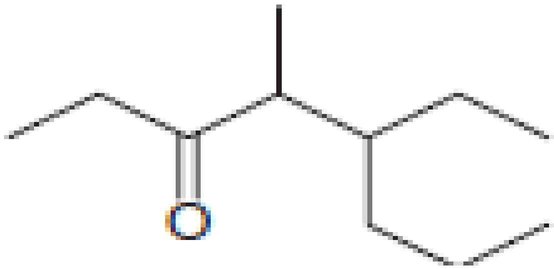
$CH_3CH_2C(=O)CH_2C(=O)CH_3$

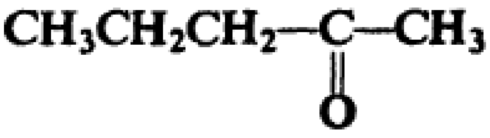
2,4-Hexanedione
(New: Hexane-2,4-dione)



$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}CH_2CH_3$

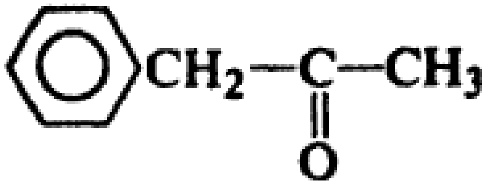
3-methyl-2-pentanone





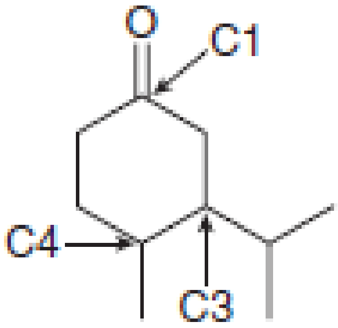
$CH_3CH_2CH_2-\underset{O}{\underset{\|}{C}}-CH_3$

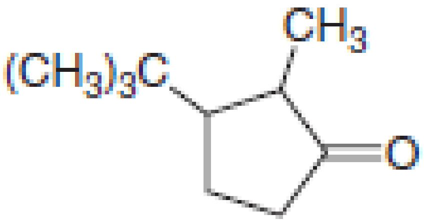
2-Pentanone



1-Phenyl-2΄-propanone

- With cyclic ketones, numbering always begins at the carbonyl carbon, but the "1" is usually omitted from the name. The ring is then numbered clockwise or counterclockwise to give the first substituent the lower number.

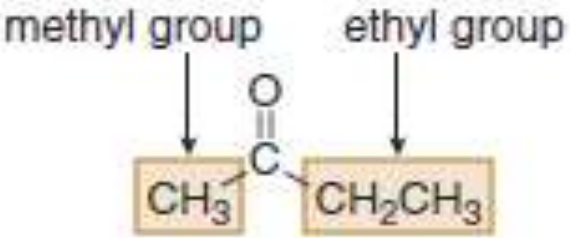




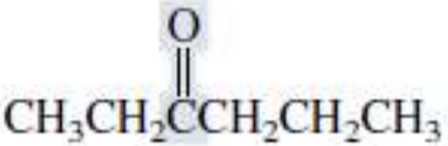
3-isopropyl-4-methylcyclohexanon

Common Names for Ketones

★ Most common names for ketones are formed by naming both alkyl groups on the carbonyl carbon, arranging them alphabetically, and adding the word *ketone*.

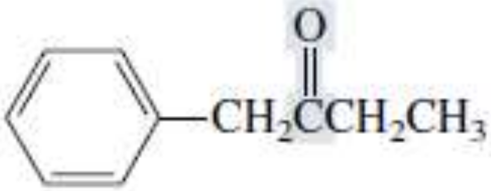


Common name: **ethyl methyl ketone**



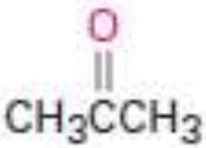
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

Ethyl propyl ketone



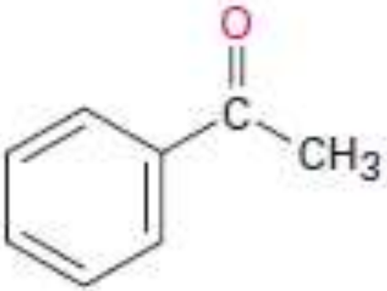
Benzyl ethyl ketone

★ A few ketones are allowed by IUPAC to retain their common names.

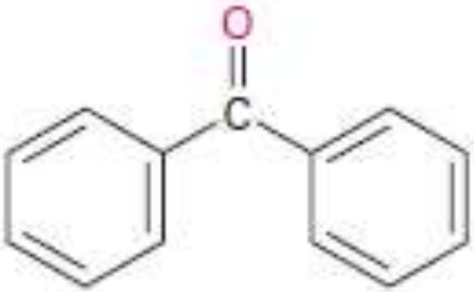


$CH_3\overset{O}{\overset{\|}{C}}CH_3$

Acetone

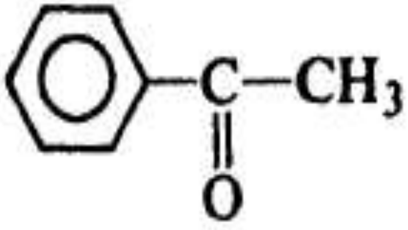


Acetophenone

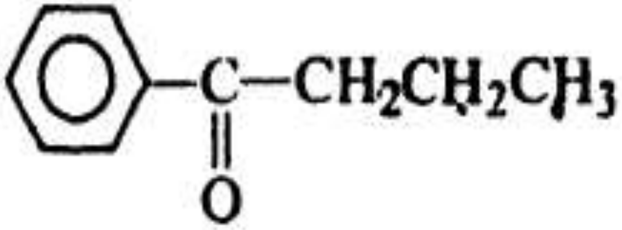


Benzophenone

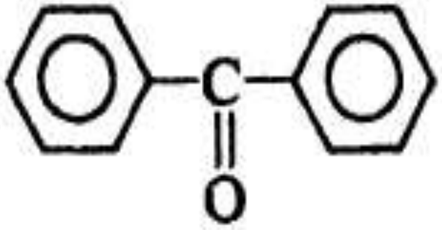
- (The suffix *-phenone* indicates that the acyl group is attached to a benzene ring.)



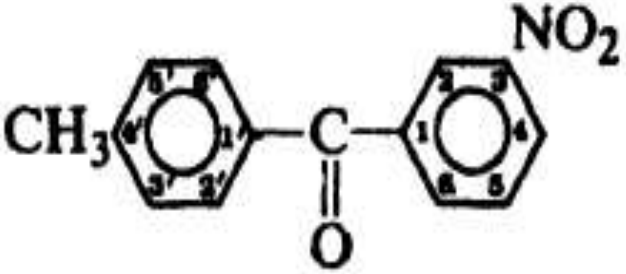
Acetophenone



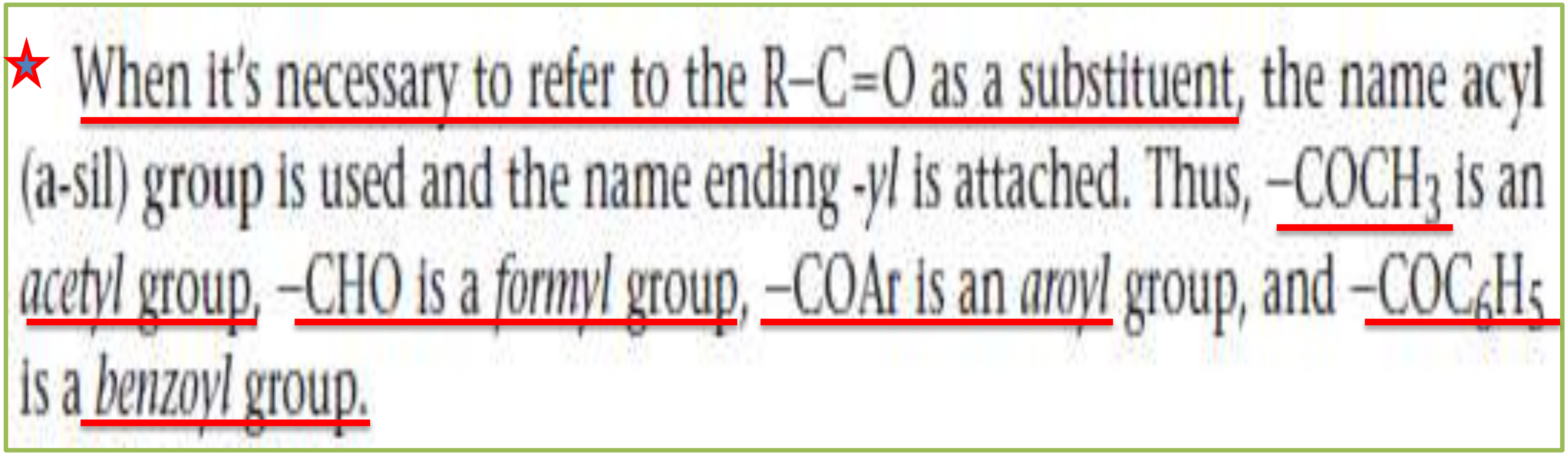
***n*-Butyrophenone**



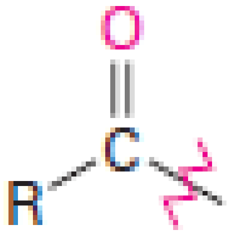
Benzophenone



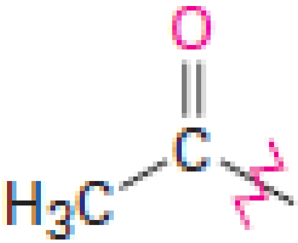
3-Nitro-4′-methylbenzophenone



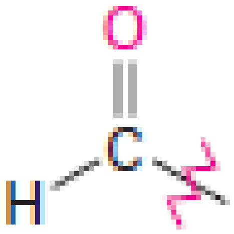
When it's necessary to refer to the R–C=O as a substituent, the name acyl (a-sil) group is used and the name ending *-yl* is attached. Thus, –$COCH_3$ is an *acetyl* group, –CHO is a *formyl* group, –COAr is an *aroyl* group, and –COC_6H_5 is a *benzoyl* group.



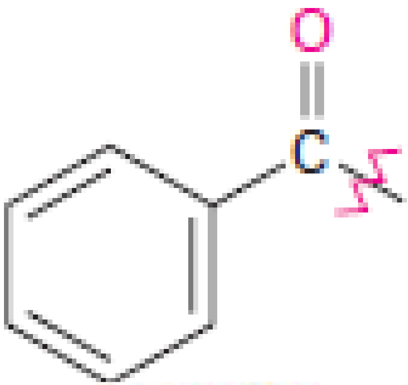
An acyl group



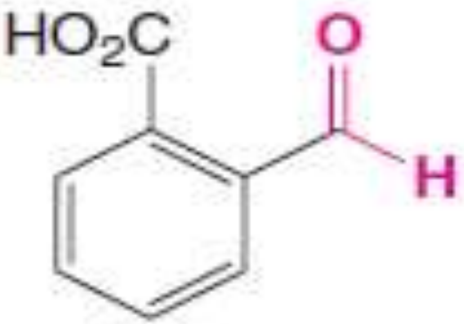
Acetyl



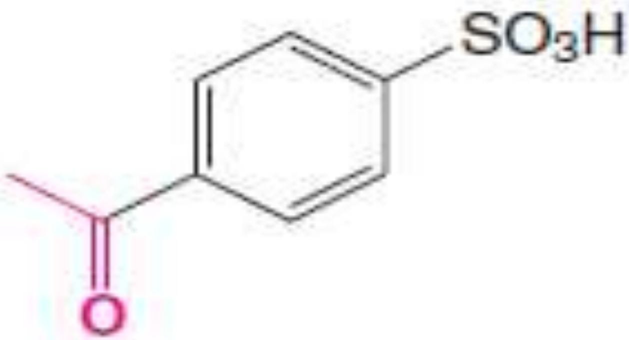
Formyl



Benzoyl

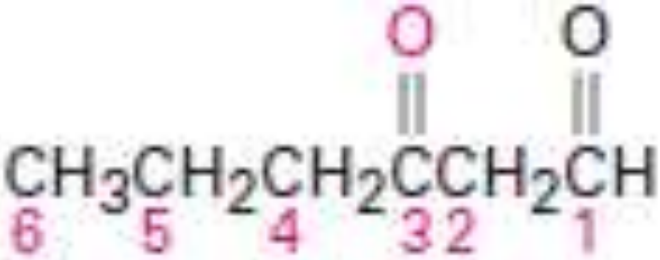


2-Methanoylbenzoic acid
(*o*-formylbenzoic acid)



4-Ethanoylbenzenesulfonic acid
(*p*-acetylbenzenesulfonic acid)

★ If other functional groups are present and the doubly bonded oxygen is considered a substituent on a parent chain, the prefix *oxo-* is used. For example:



$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{\overset{\overset{O}{\|}}{C}}\underset{2}{CH_2}\underset{1}{\overset{\overset{O}{\|}}{C}H}$

3-Oxohexanal

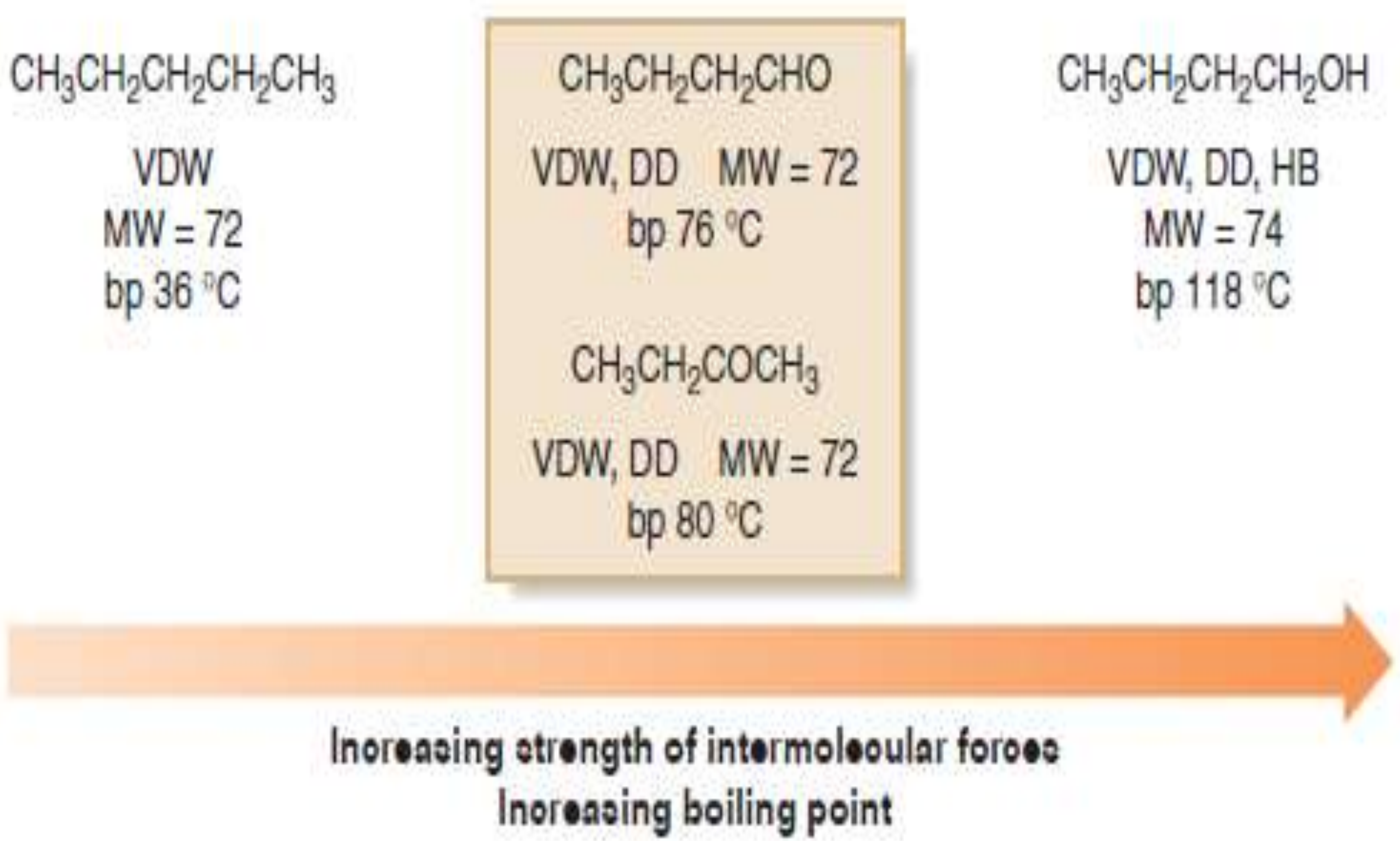
Physical Properties (B.P.s)

1- The Presence of Polar carbonyl group makes Aldehydes and Ketones polar compounds ; therefore they have higher B.P.s than non polar compounds of comparable molecular weight.

2- They are not capable of intermolecular H- bonding. As a results they have lower boiling than corresponding alcohols of the same molecular weights

Physical Properties of Aldehydes and Ketones

- For compounds of comparable molecular weight, bp's and mp's follow the usual trend: The stronger the intermolecular forces, the higher the bp or mp.



$CH_3CH_2CH_2CH_2CH_3$

VDW
MW = 72
bp 36 °C

$CH_3CH_2CH_2CHO$

VDW, DD MW = 72
bp 76 °C

$CH_3CH_2COCH_3$

VDW, DD MW = 72
bp 80 °C

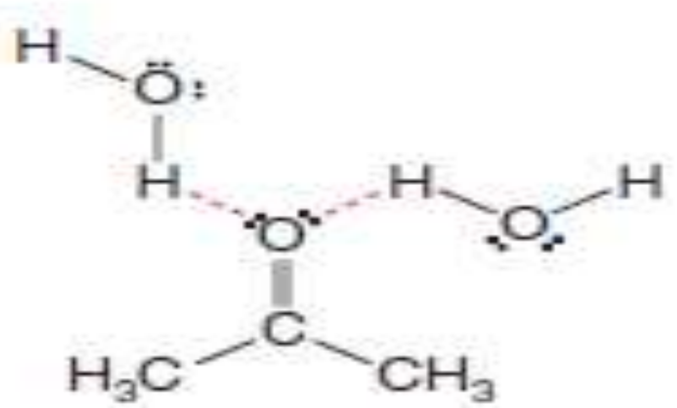
$CH_3CH_2CH_2CH_2OH$

VDW, DD, HB
MW = 74
bp 118 °C

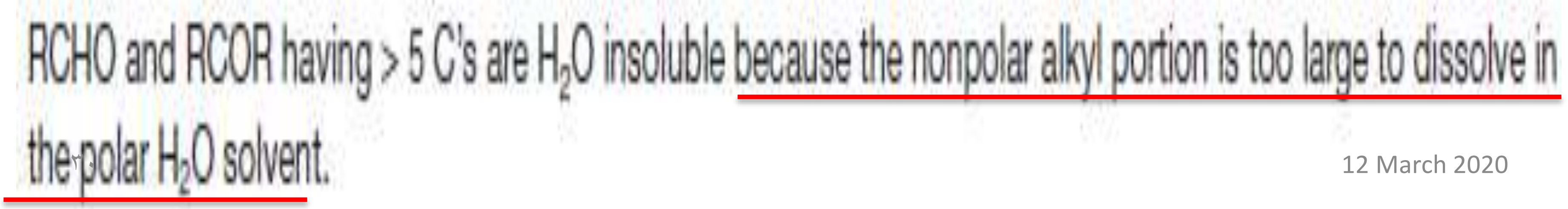
Increasing strength of intermolecular forces
Increasing boiling point

Solubility

3- The lower **aldehydes** and **ketones** are soluble in water because of H-bonding with water. They are all soluble in organic solvents



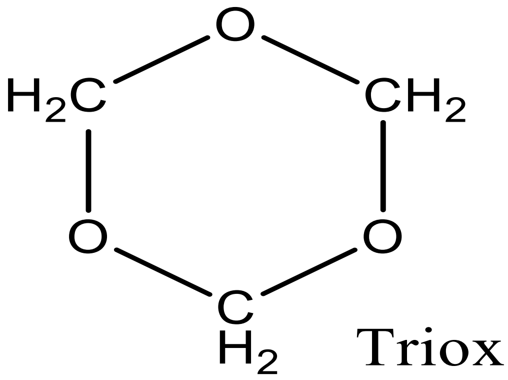
Hydrogen bonding (shown in red) between water molecules and acetone



RCHO and RCOR having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent.

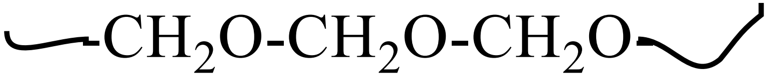
4- **Formaldehyde** is gas (b.p. = -25 and is use either as aqueous solution (formalin) or as one of its solid polymers

- paraformaldehyde $(-CH_2O-)_n$
- Trioxane $(CH_2O)_3$



Trioxane

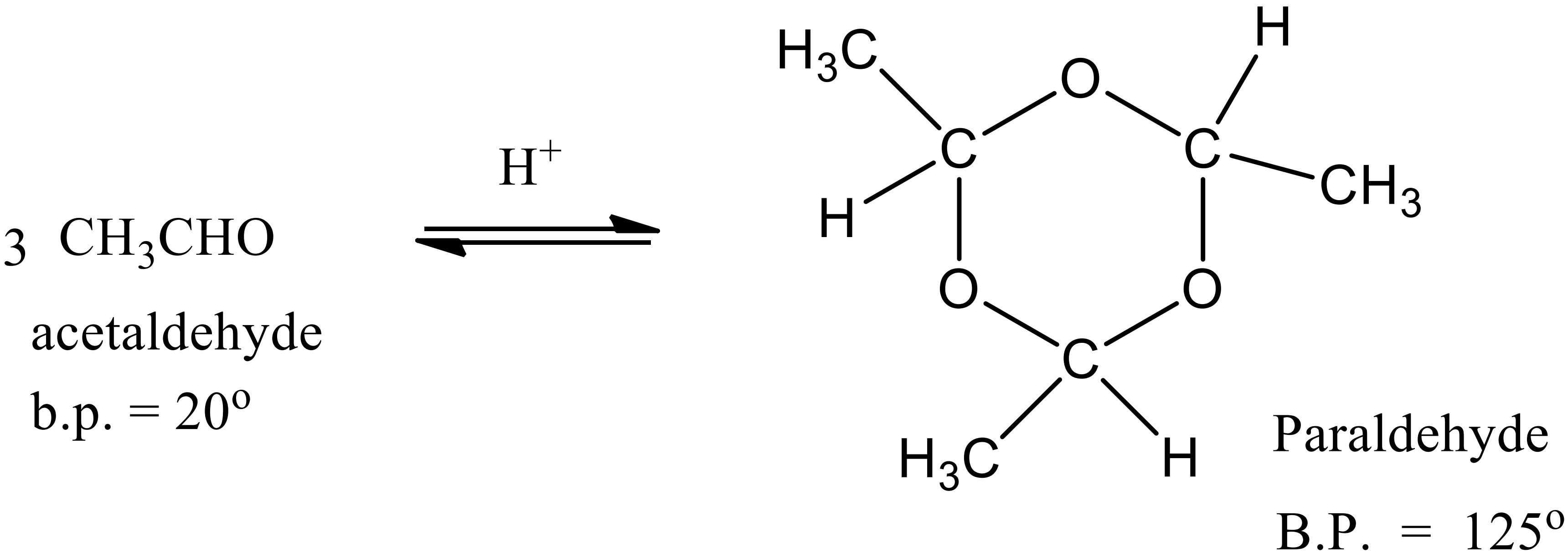
Metaformaldehyde



$$-CH_2O-CH_2O-CH_2O-$$

Paraformaldehyde

- Acetaldehyde (b.p. =20) is often generated from its higher boiling trimer by heating with acid:



$3\ CH_3CHO \xrightleftharpoons{H^+}$

acetaldehyde

b.p. = 20^o

Paraldehyde

B.P. = 125^o

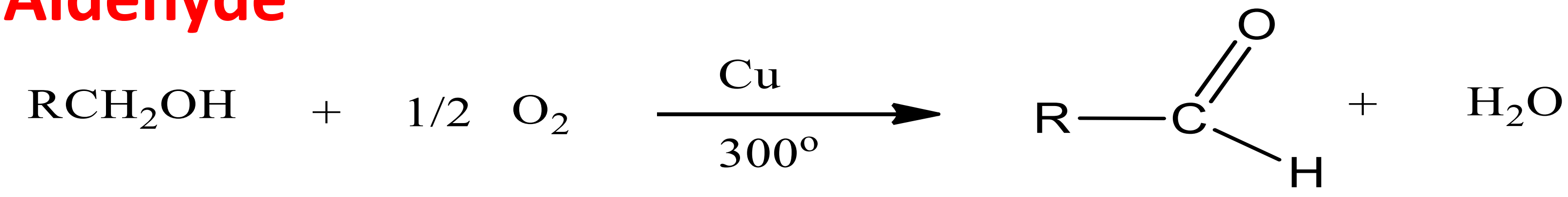
Preparation of Aldehydes and Ketones

1- Industrial Preparation of aldehydes:

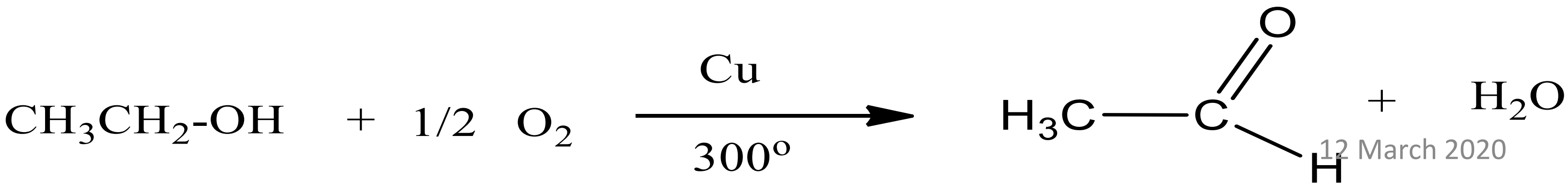
The presence of aldehydes and ketones in natural products, (vaniline, cinamone, almondes,…etc.) and involved in many organic reactions, encourage scientists to find industrial methods:

A- Oxidation of primary alcohols or

Alcohol Dehydrogenation, which give the name **Aldehyde**

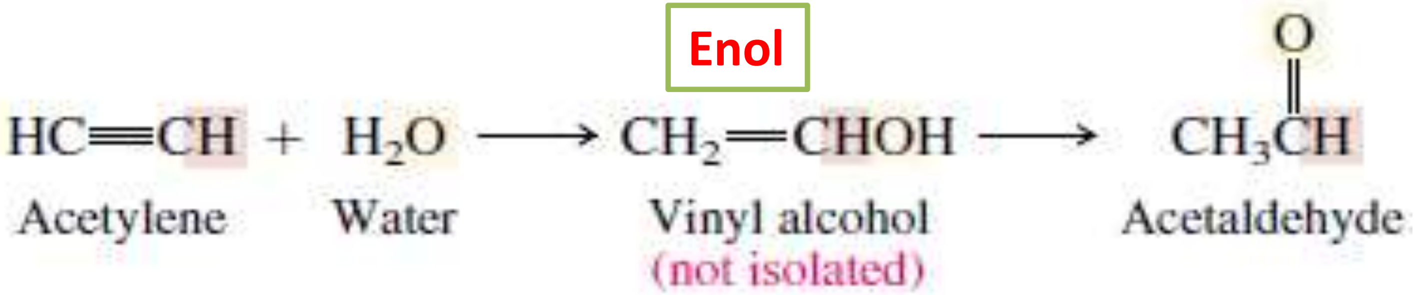


Ex/



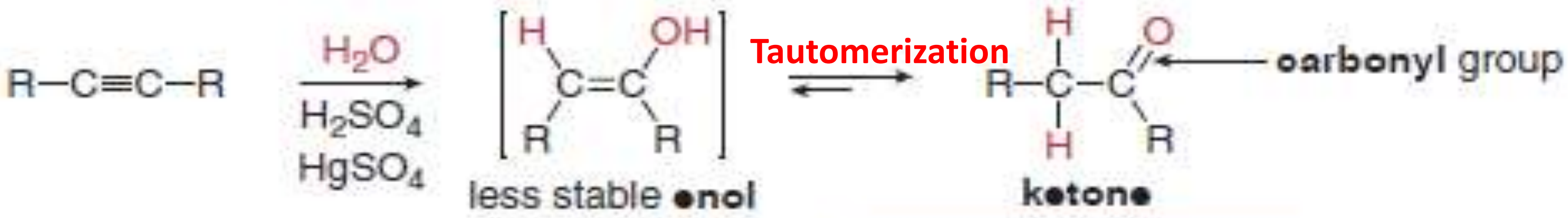
B- Hydration of Acetylene in the presence of $HgSO_4$, H_2SO_4

Because of the regioselectivity of alkyne hydration, acetylene is the only alkyne structurally capable of yielding an aldehyde under these conditions.



$$HC{\equiv}CH + H_2O \longrightarrow CH_2{=}CHOH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$$

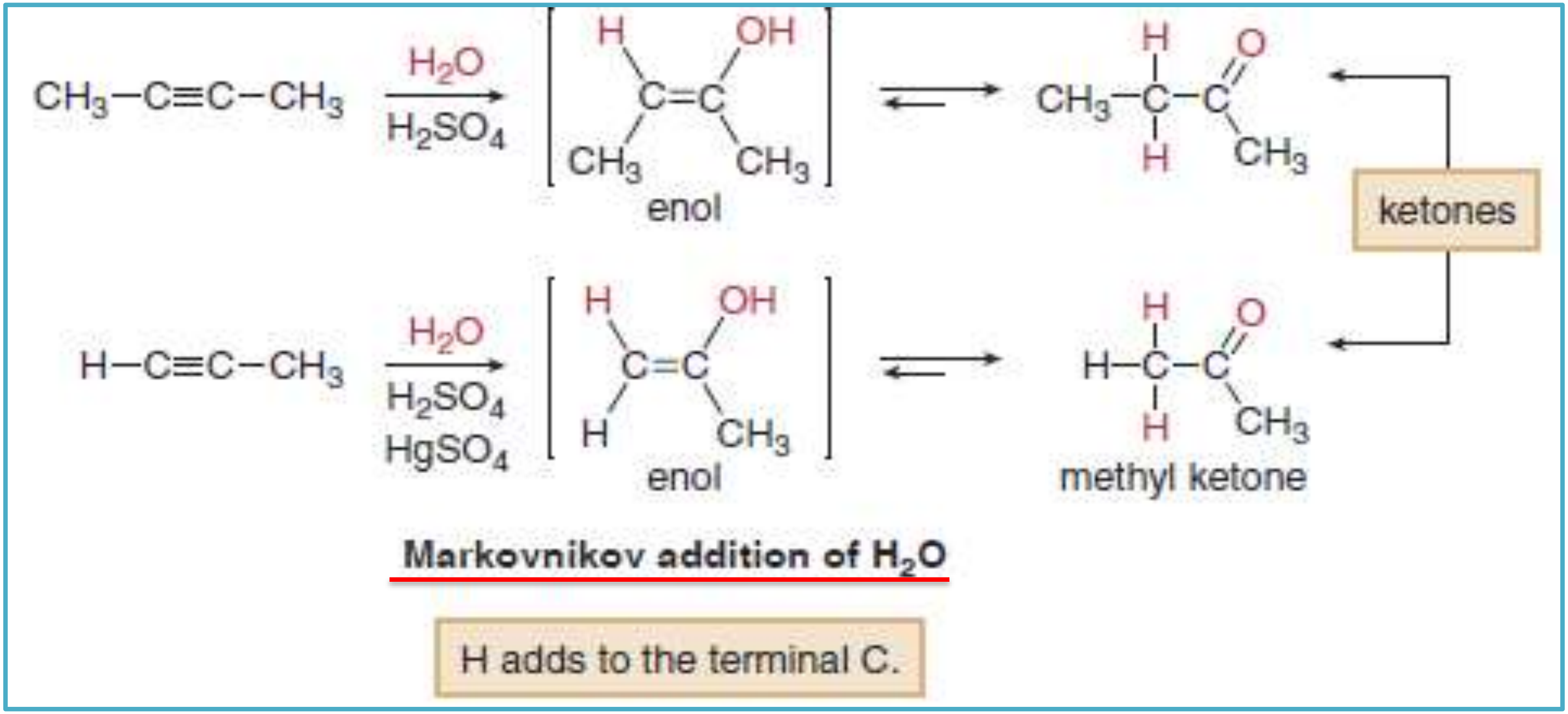
At one time acetaldehyde was prepared on an industrial scale by this method. Modern methods involve direct oxidation of ethylene and are more economical.



H_2O has been added.

- *Tautomers* are constitutional isomers that differ in the location of a double bond and a hydrogen atom. Two tautomers are in equilibrium with each other.

Internal alkynes undergo hydration with concentrated acid, whereas terminal alkynes require the presence of an additional Hg^{2+} catalyst—usually $HgSO_4$—to yield methyl ketones by Markovnikov addition of H_2O.



Lab. Syntheses of Aldehydes

1- Oxidation of 1° Alcohols ,

using $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ with H_2SO_4,
or PCC in CH_2Cl_2 at room temp.
or I(v)-containing *Dess-Martin periodinane* in CH_2Cl_2 solvent

Example:

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{PCC in } CH_2Cl_2]{K_2Cr_2O_7,\ H_2SO_4,\ \text{warm}} CH_3CH_2CH_2CHO$$

n-Butyl alcohol
(1-Butanol)
B.p. 118°

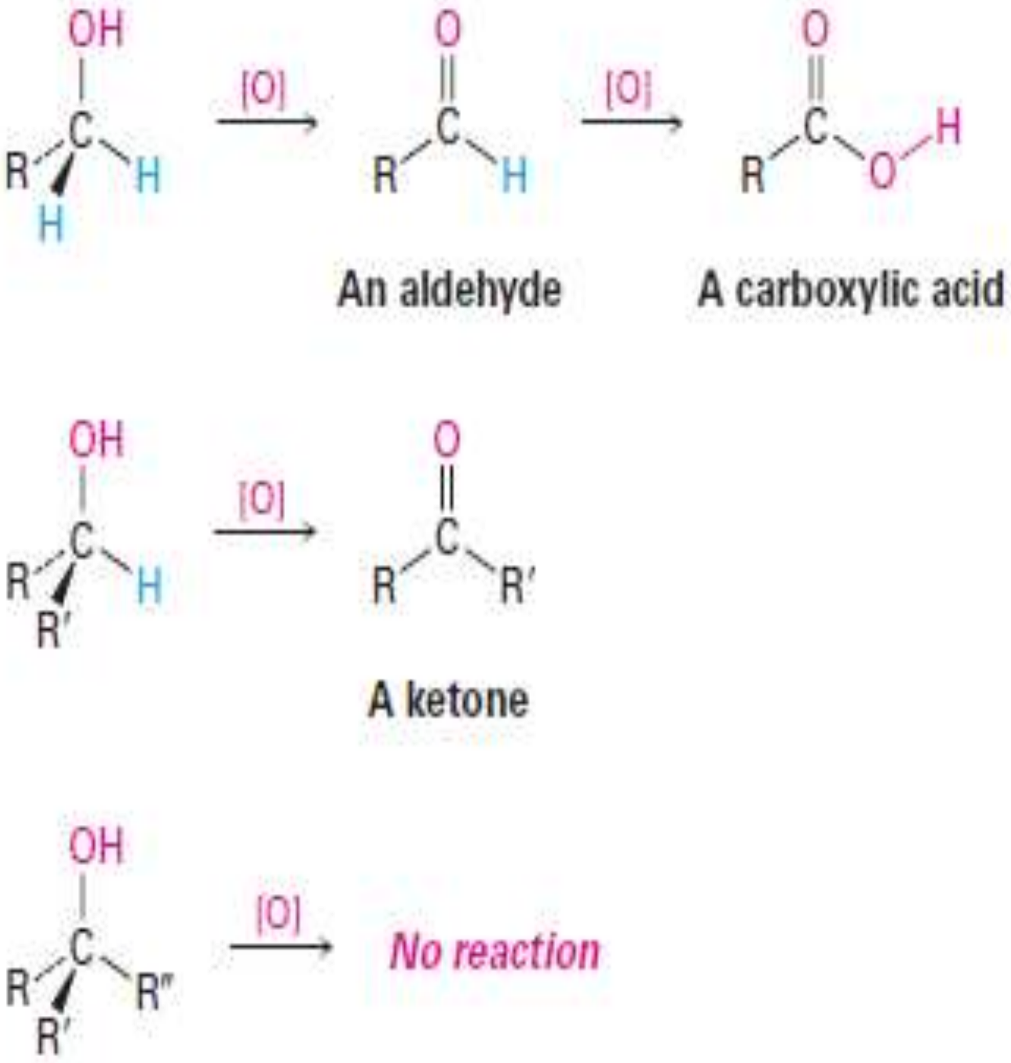
n-Butyraldehyde
(Butanal)
B.p. 76°

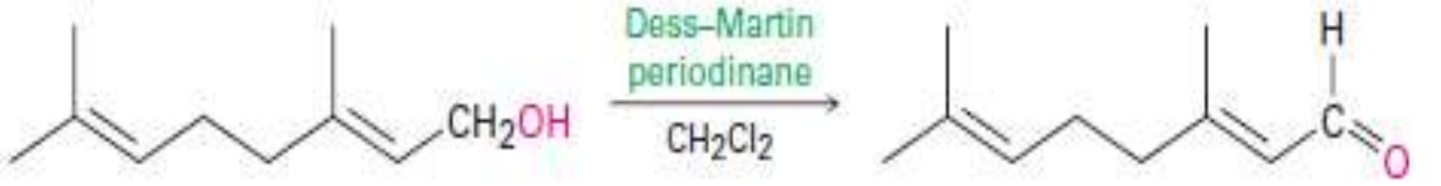
Distillation from reaction mixture

Primary alcohol

Secondary alcohol

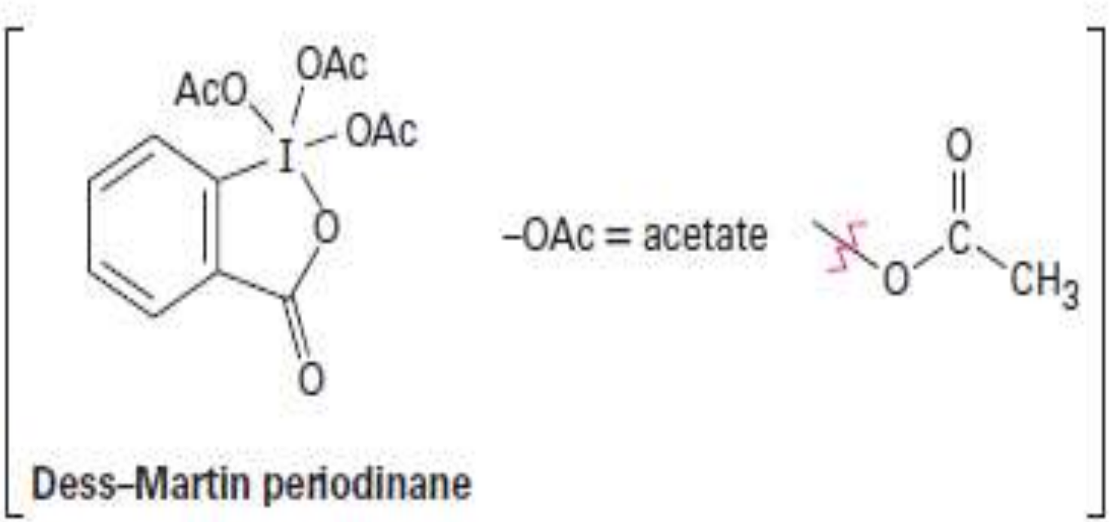
Tertiary alcohol



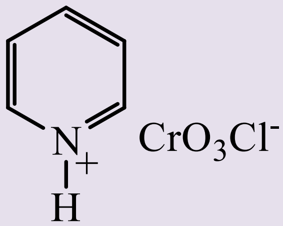


Geraniol

Geranial (84%)



Dess–Martin periodinane



Pyridinium Chlorochromate (PCC)
Prepared by disolving CrO_3 in HCl
Followed by treatment with pyridine.

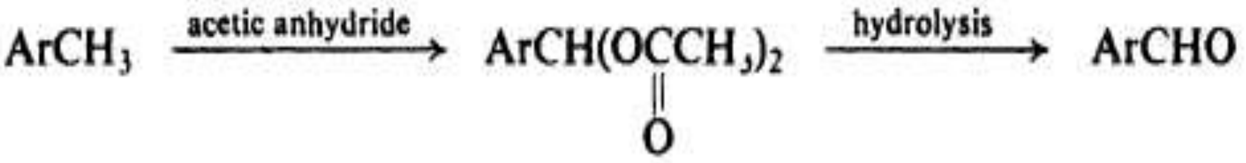
Selective oxidation of primary alcohols to Aldehydes ONLY no further
Also known as Corey's reagent. Does not oxidize aldehydes to acids.

2- Oxidation of methyl benzene.

Toluene oxidized with permanganate **$KMnO_4$** give Benzoic acid.

Partial oxidation gives Aldehyde:

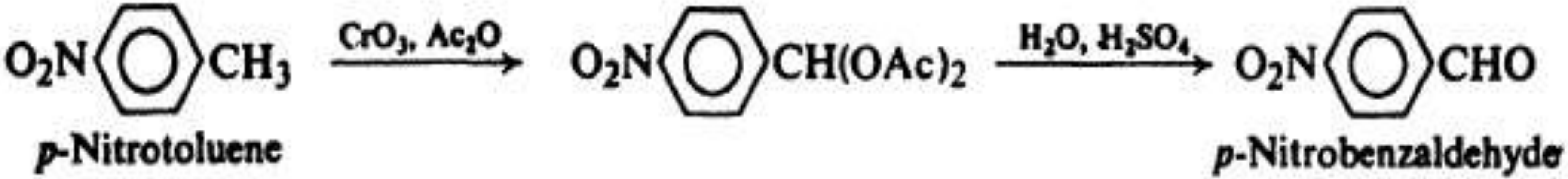
A- Use of acetic anhydride, to give gem-diacetate , hydrolysis give ald.



$$ArCH_3 \xrightarrow{\text{acetic anhydride}} ArCH(O\underset{\underset{\displaystyle O}{\|}}{C}CH_3)_2 \xrightarrow{\text{hydrolysis}} ArCHO$$

A *gem*-diacetate
Not oxidized

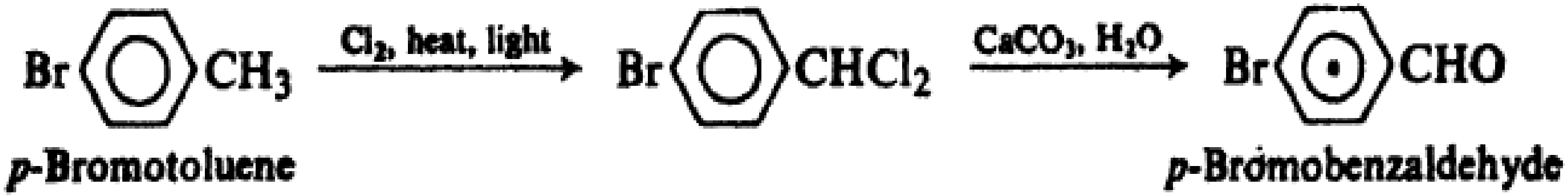
Gem = Twin



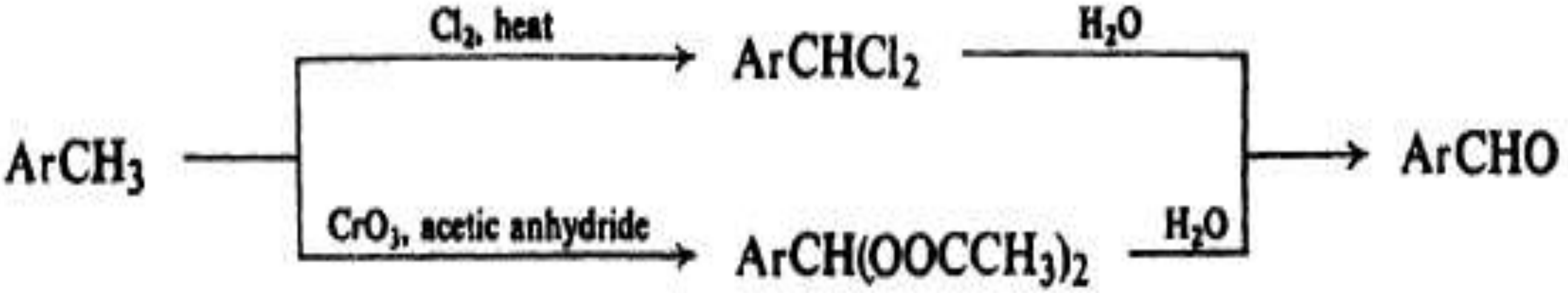
$O_2N\text{-}C_6H_4\text{-}CH_3 \xrightarrow{CrO_3,\ Ac_2O} O_2N\text{-}C_6H_4\text{-}CH(OAc)_2 \xrightarrow{H_2O,\ H_2SO_4} O_2N\text{-}C_6H_4\text{-}CHO$

B- Hydration of Dihalogen Compounds
Gem-Dihalides:

Examples:

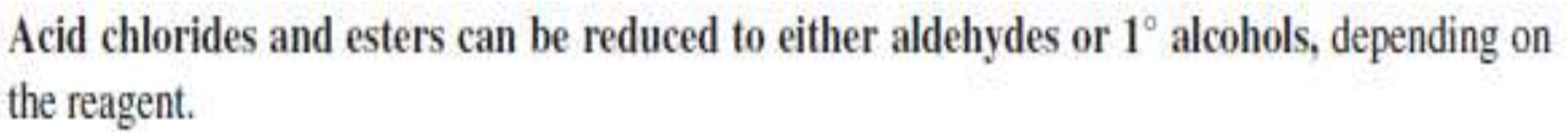


So using either Cl_2 or CrO_3/ Acetic anhydride

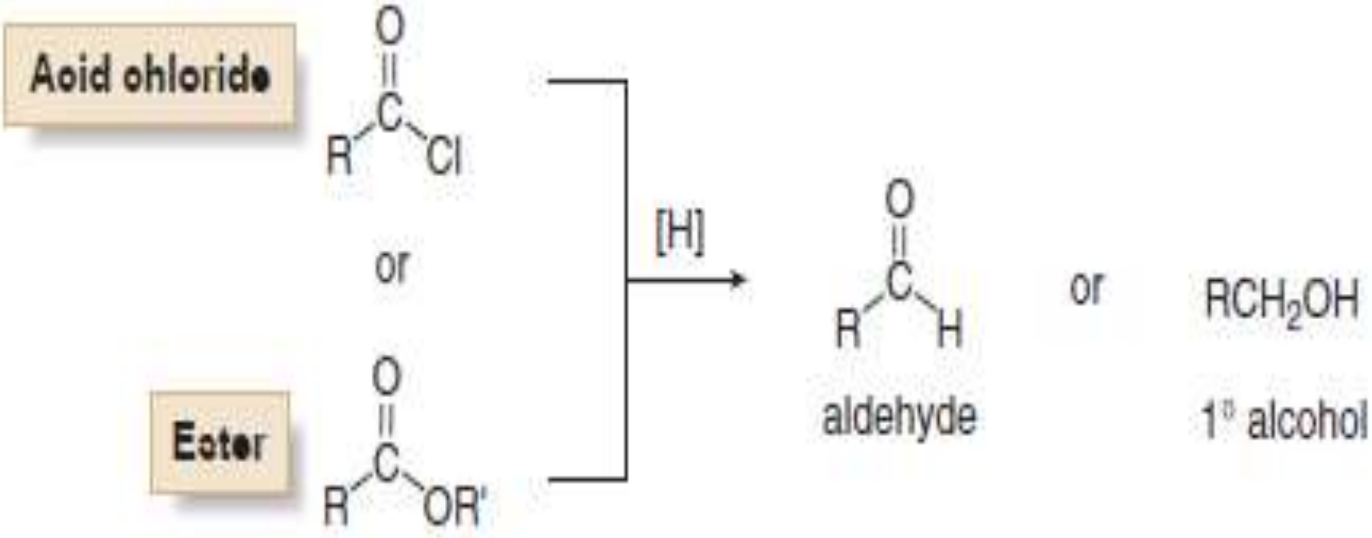


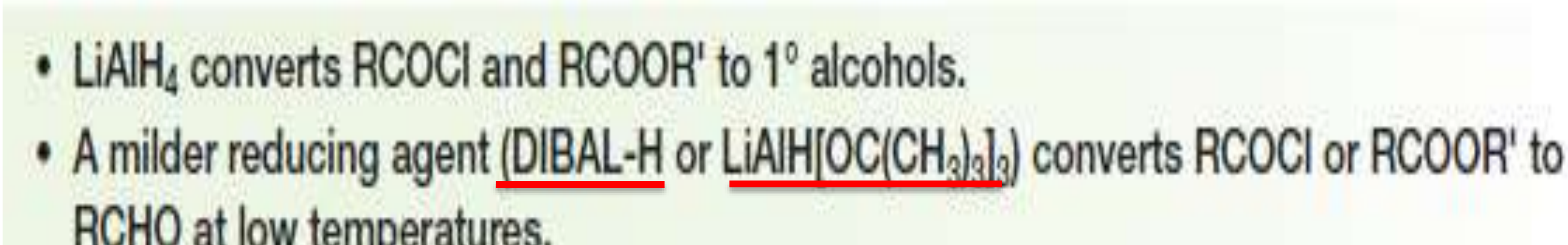
3- Reduction of Acid Chlorides and Esters:

A- Reduction of acid chlorides



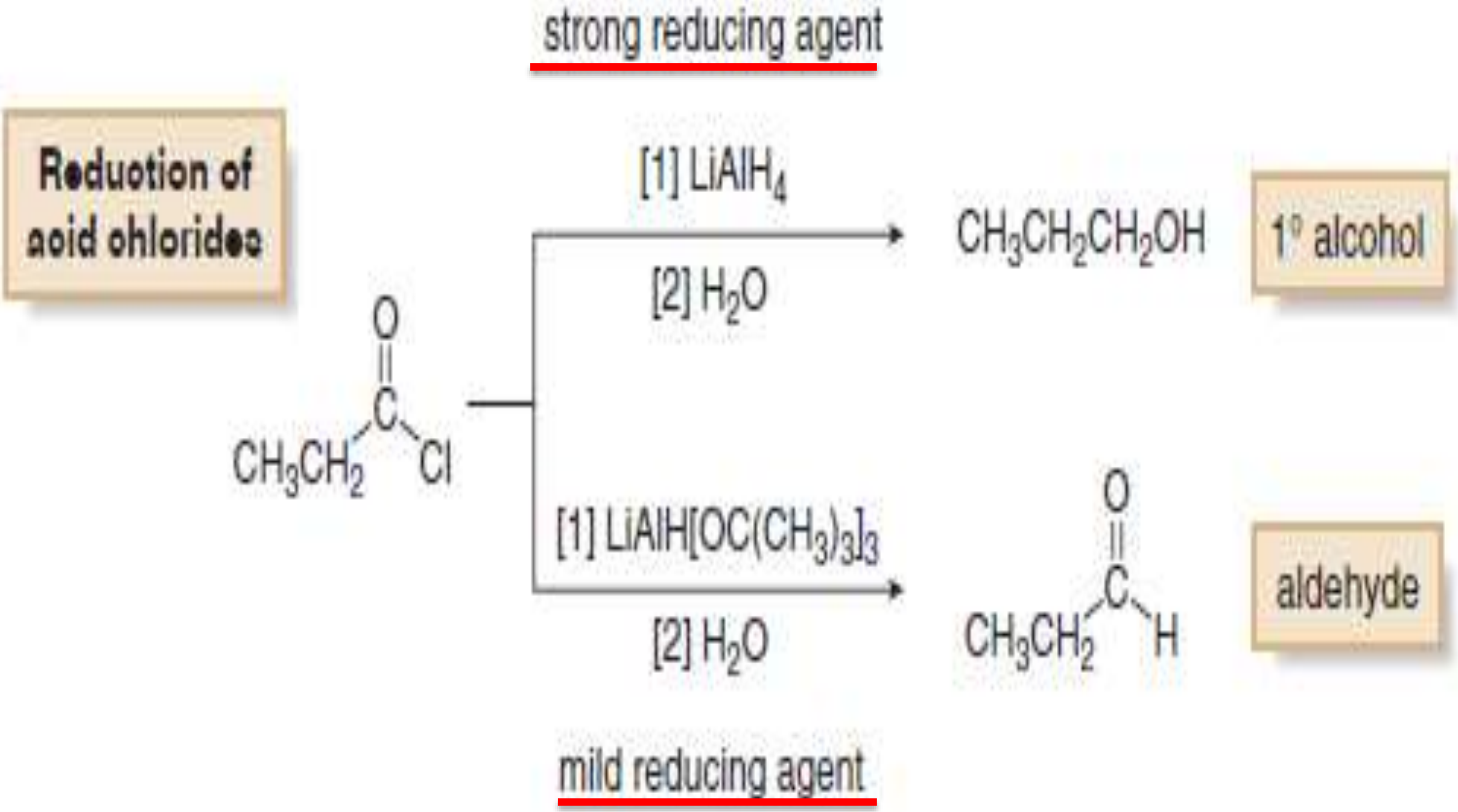
Acid chlorides and esters can be reduced to either aldehydes or 1° alcohols, depending on the reagent.





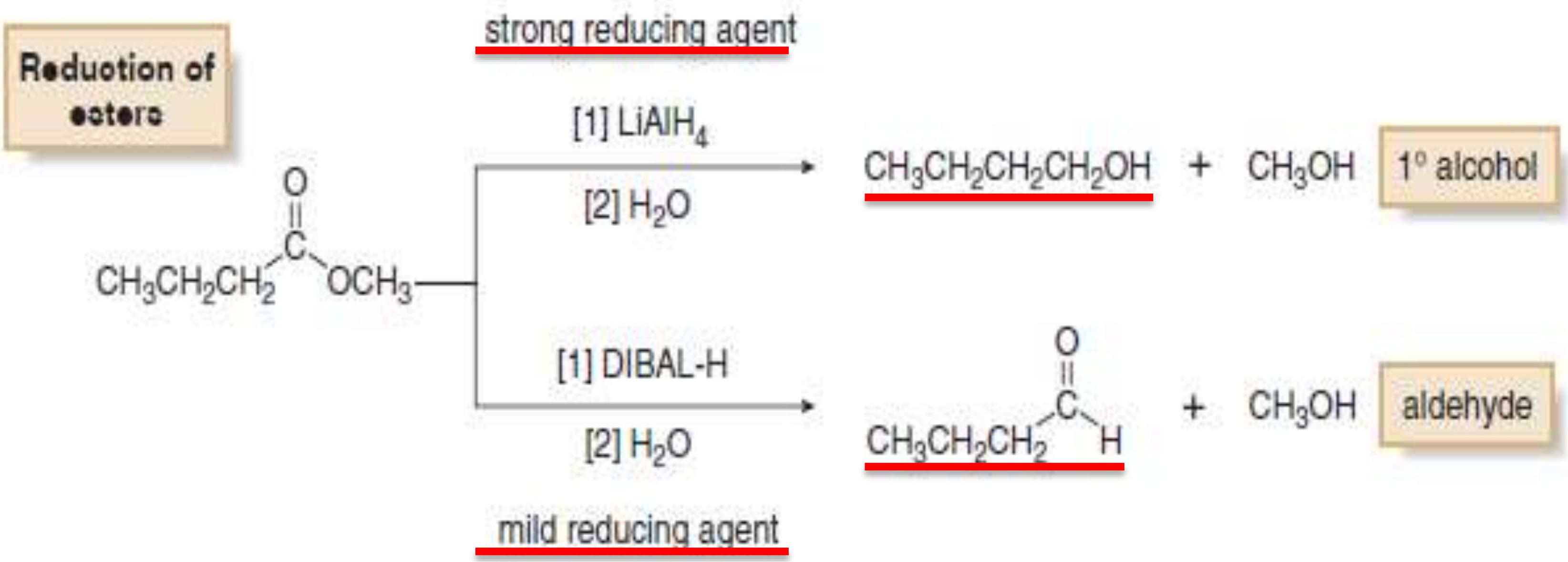
- $LiAlH_4$ converts RCOCl and RCOOR' to 1° alcohols.
- A milder reducing agent (DIBAL-H or $LiAlH[OC(CH_3)_3]_3$) converts RCOCl or RCOOR' to RCHO at low temperatures.

Examples:



In the reduction of an acid chloride, Cl^- comes off as the leaving group.

B- reduction of esters:

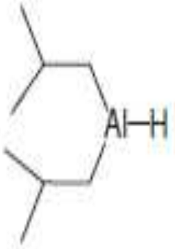


$$CH_3CH_2CH_2COOCH_3 \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} CH_3CH_2CH_2CH_2OH + CH_3OH$$

$$CH_3CH_2CH_2COOCH_3 \xrightarrow[\text{[2] } H_2O]{\text{[1] DIBAL-H}} CH_3CH_2CH_2CHO + CH_3OH$$

In the reduction of the ester, CH_3O^- comes off as the leaving group, which is then protonated by H_2O to form CH_3OH.

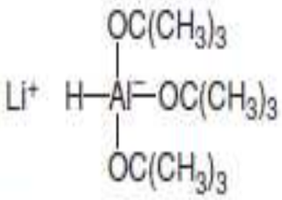
$LiAlH_4$ is a strong, nonselective reducing agent. DIBAL-H and $LiAlH[OC(CH_3)_3]_3$ are milder, more selective reducing agents.



= $[(CH_3)_2CHCH_2]_2AlH$

diisobutylaluminum hydride

DIBAL-H



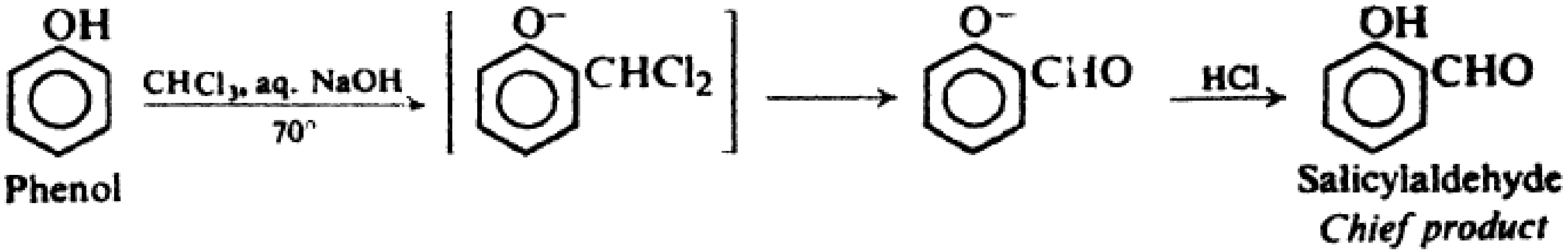
$Li^+\ H{-}\overset{OC(CH_3)_3}{\underset{OC(CH_3)_3}{Al^-}}{-}OC(CH_3)_3$ = $LiAlH[OC(CH_3)_3]_3$

lithium tri-*tert*-butoxyaluminum hydride

4- Reimer-Tiemann Reaction:

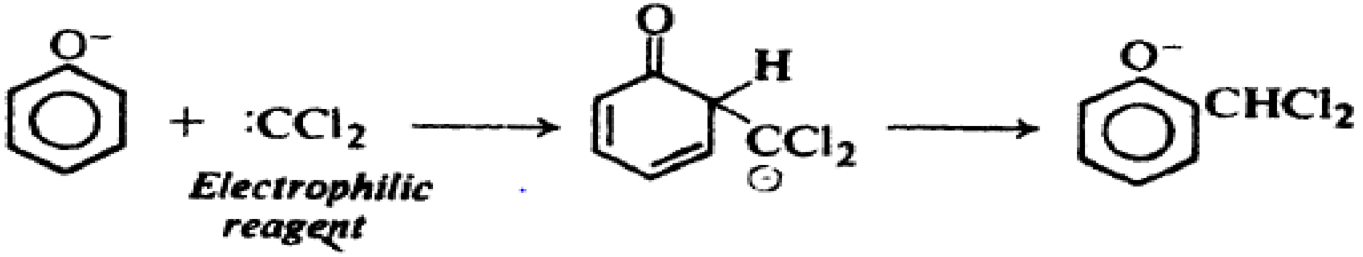
Synthesis of Phenolic Aldehydes. Dichlorocarbene

Treatment of a phenol with chloroform and aqueous hydroxide introduces an aldehyde group, —CHO, into the aromatic ring, generally *ortho* to the —OH. This reaction is known as the **Reimer-Tiemann reaction**. For example:



A substituted benzal chloride is initially formed, but is hydrolyzed by the alkaline reaction medium.

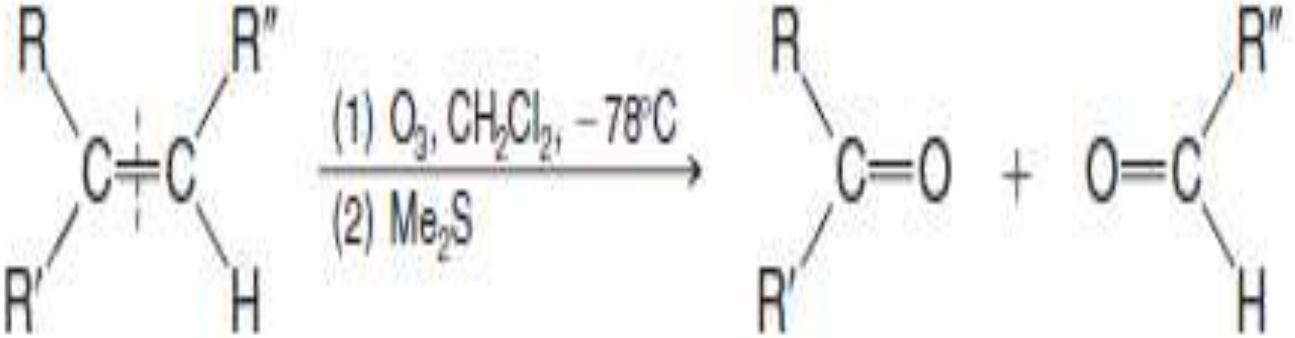
$$\underset{\text{Chloroform}}{OH^- + CHCl_3} \rightleftharpoons H_2O + {}^-{:}CCl_3 \longrightarrow Cl^- + \underset{\text{Dichlorocarbene}}{:CCl_2}$$



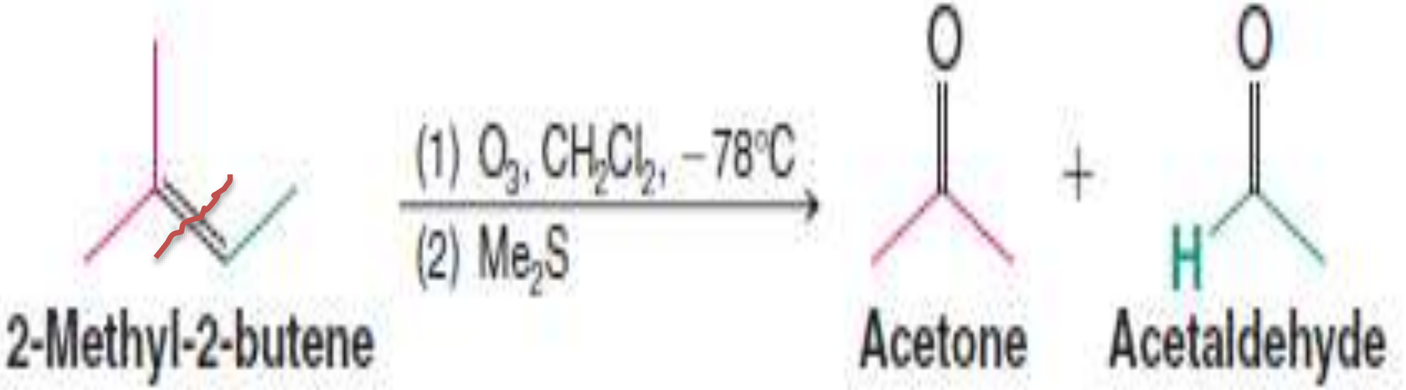
5- Ozonolysis of alkene, gives Ald. & Ketones

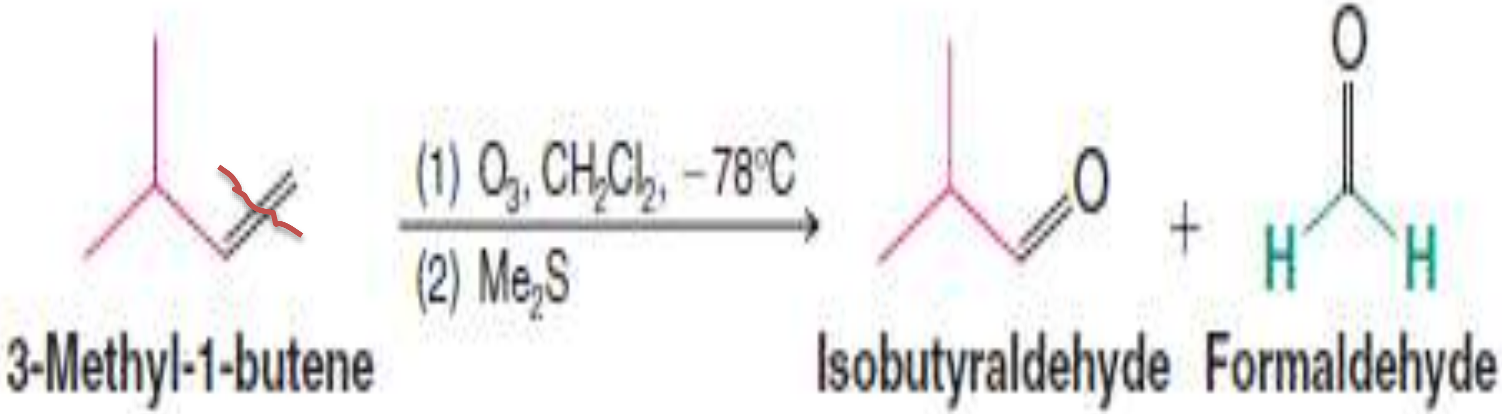
- The most useful method for cleaving alkenes is to use ozone (O_3).

Ozonolysis consists of bubbling ozone into a very cold (−78°C) solution of the alkene in CH_2Cl_2, followed by treatment of the solution with dimethyl sulfide (or zinc and acetic acid). The overall result is as follows:



The following examples illustrate the results for each type of alkene carbon.

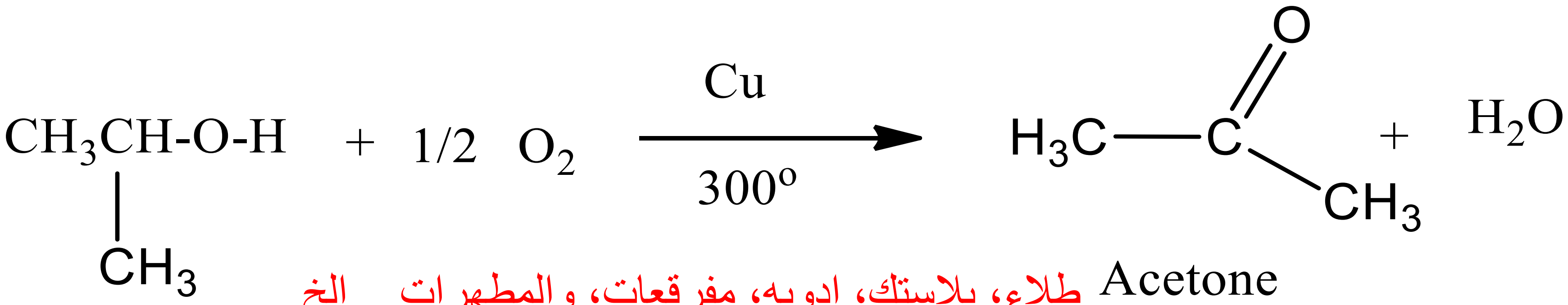




Preparation of Ketones:
1- Oxidation of 2° Alcohols

2° Alcohols oxidized to give ketones

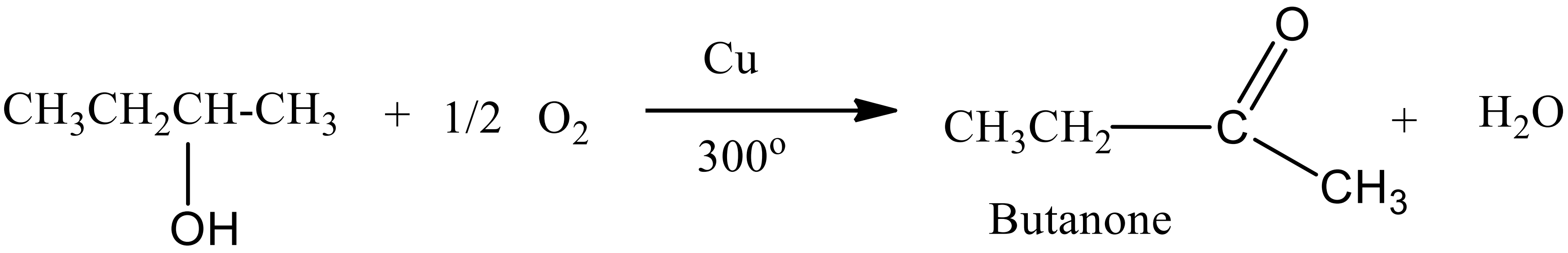
Using Cu and Air at 300°C : Industrial



$$\underset{CH_3}{CH_3CH\text{-}O\text{-}H} + 1/2\ O_2 \xrightarrow[300^o]{Cu} H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H_2O$$

Acetone

طلاء، بلاستك، ادويه، مفرقعات، و المطهرات....الخ



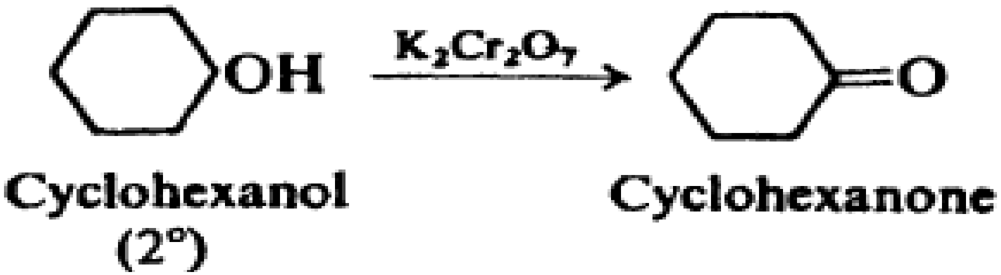
$$\underset{OH}{CH_3CH_2CH\text{-}CH_3} + 1/2\ O_2 \xrightarrow[300^o]{Cu} CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H_2O$$

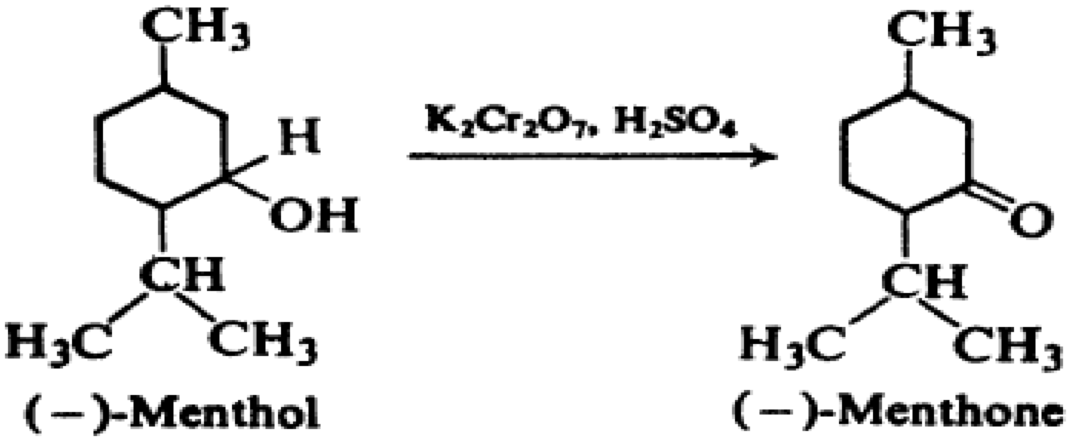
Butanone

2° Alcohols also oxidized to Ketones using Chromic acid or CrO_3 in glacial acetic acid:

$$\text{Secondary:}\quad R-\overset{R}{\overset{|}{C}}HOH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3} R-\overset{R}{\overset{|}{C}}=O$$

A ketone



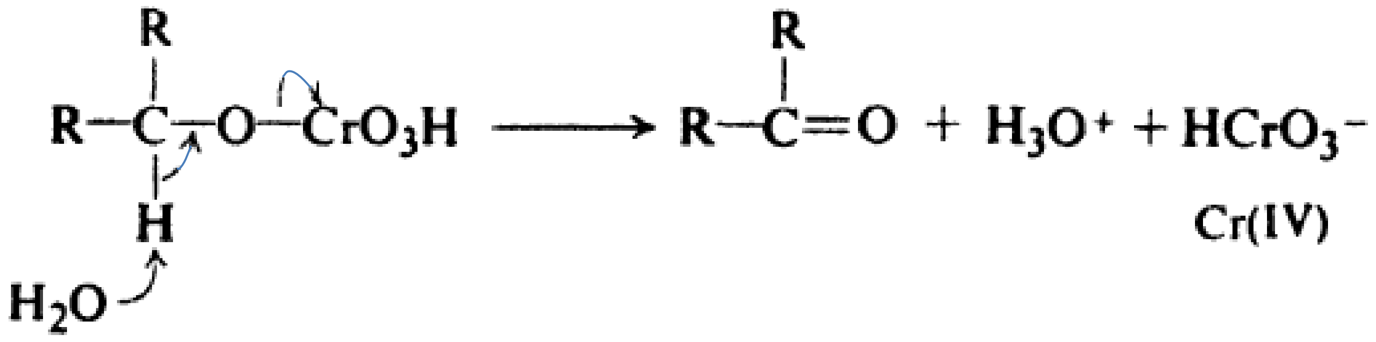


Possible Mechanism

(1) $$R_2CHOH + \underset{Cr(VI)}{HCrO_4^-} + H^+ \longrightarrow R_2CHOCrO_3H + H_2O$$

Chromate ester

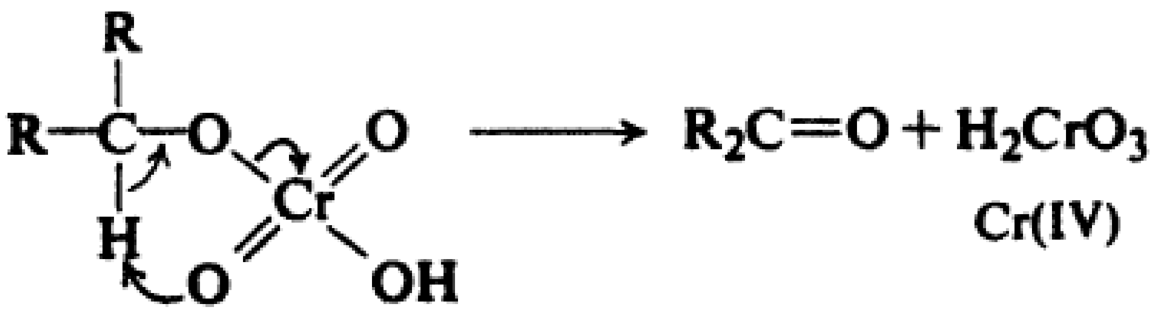
(2)



$$R_2CH{-}O{-}CrO_3H + H_2O \longrightarrow R_2C{=}O + H_3O^+ + \underset{Cr(IV)}{HCrO_3^-}$$

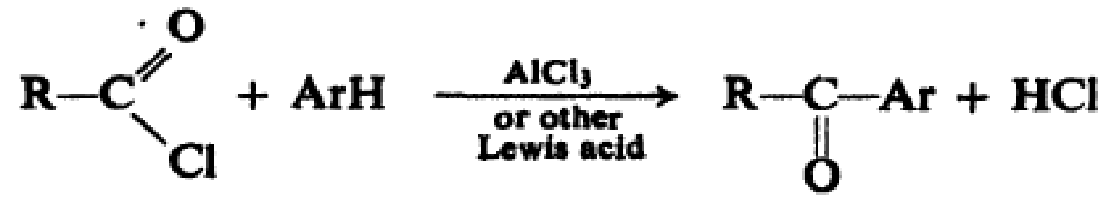
It is possible that the proton is lost to an oxygen of the ester group in a cyclic mechanism **2a**

(2a)



$$R_2CH{-}O{-}Cr(=O)_2OH \longrightarrow R_2C{=}O + \underset{Cr(IV)}{H_2CrO_3}$$

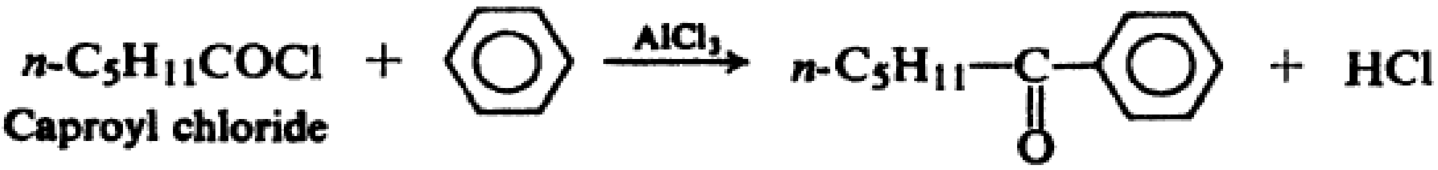
2- Friedel-Crafts Acylation



Acid chloride

Ketone

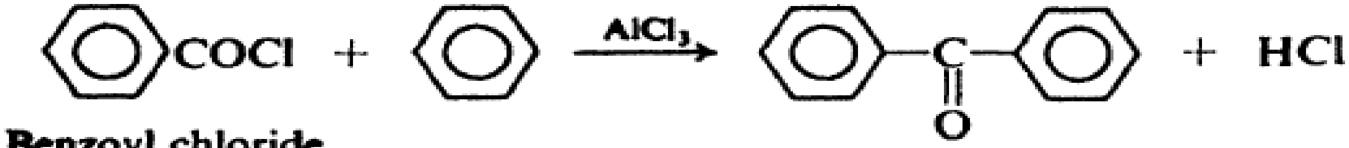
Examples:



Caproyl chloride

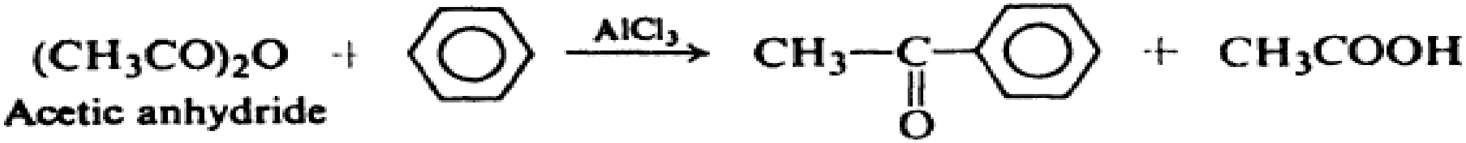
n-Pentyl phenyl ketone

No rearrangement of n-pentyl group



Benzoyl chloride

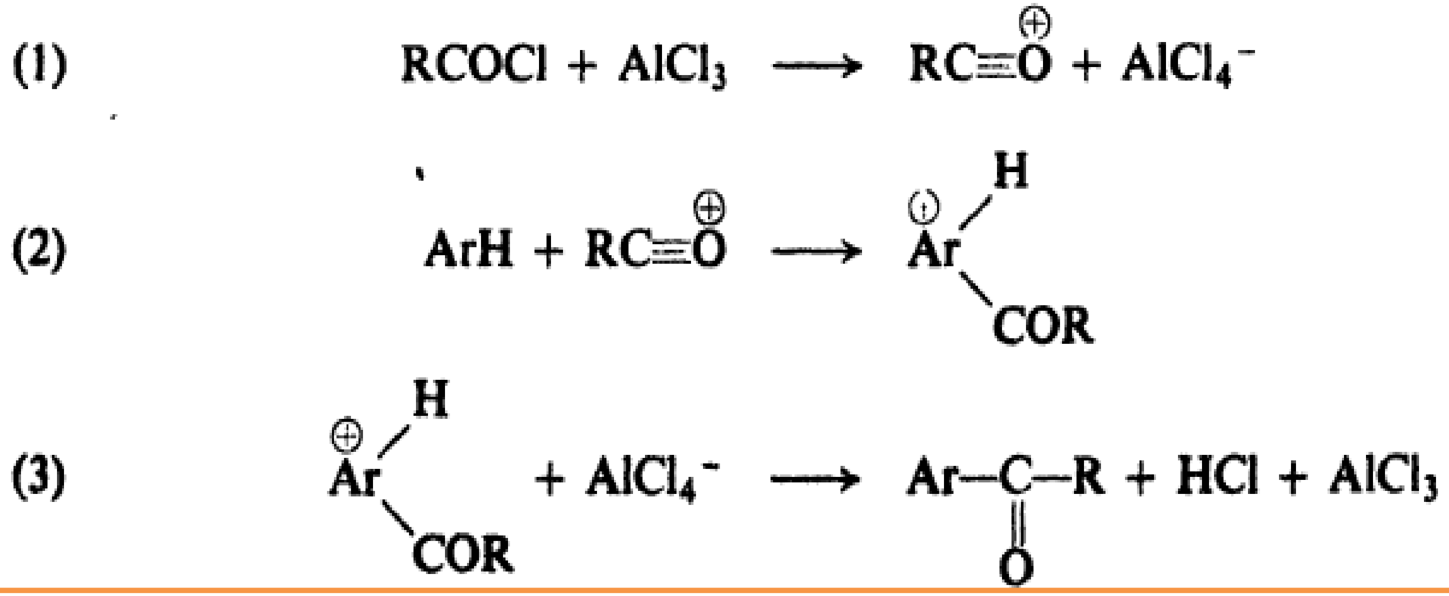
Benzophenone
(Phenyl ketone)



Acetic anhydride

Acetophenone
(Methyl phenyl ketone)

The most likely mechanism for Friedel-Crafts acylation is analogous to the carbonium ion mechanism for Friedel-Crafts alkylation (Sec. 11.10), and involves the following steps:

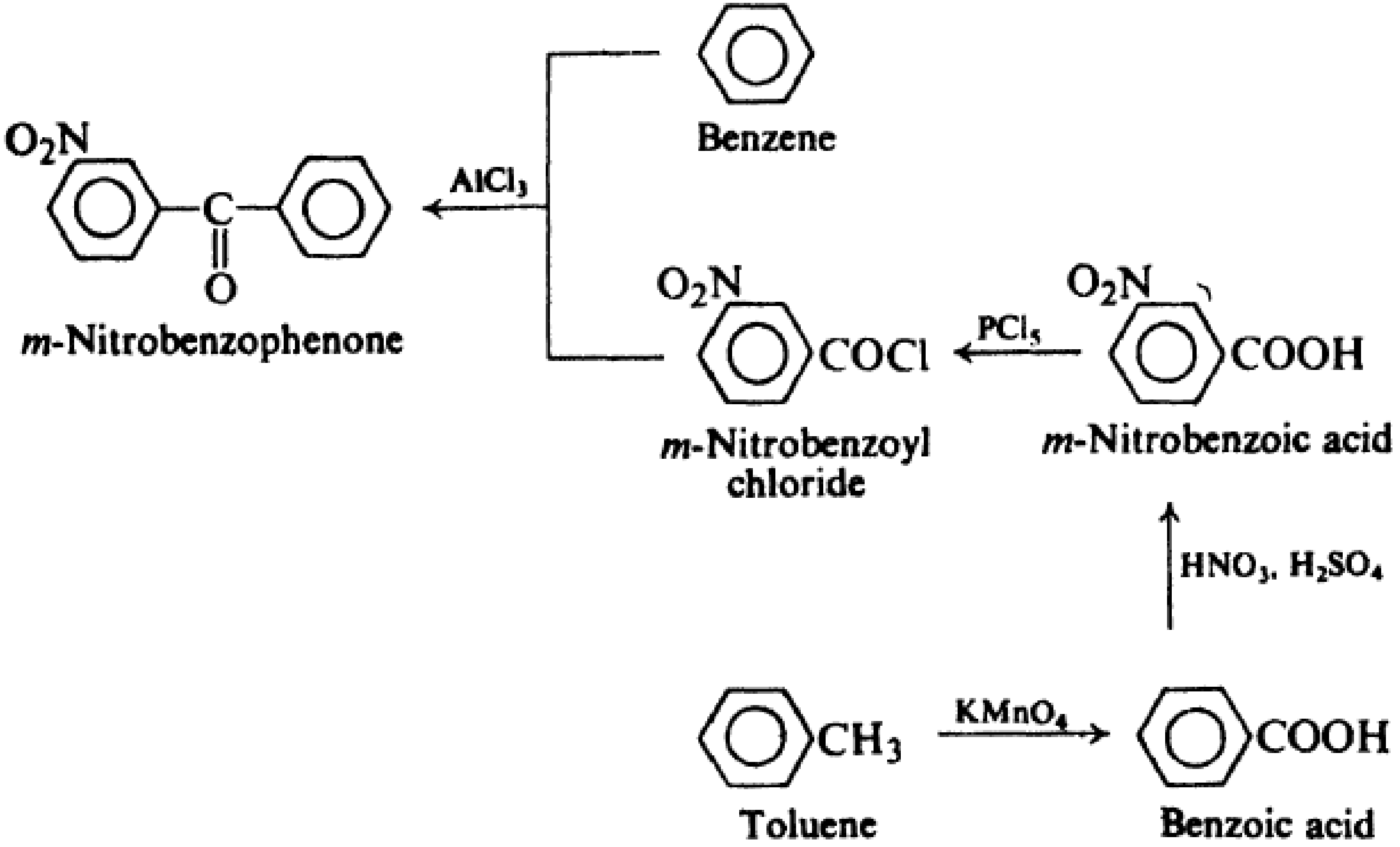


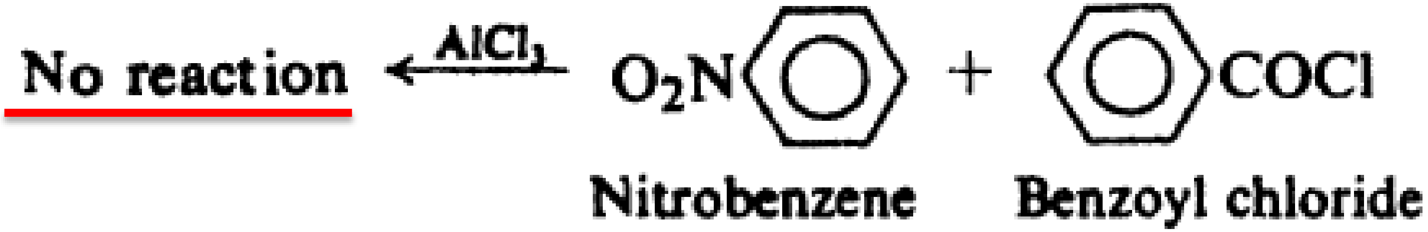
(1) $RCOCl + AlCl_3 \longrightarrow RC{\equiv}\overset{\oplus}{O} + AlCl_4^-$

(2) $ArH + RC{\equiv}\overset{\oplus}{O} \longrightarrow \overset{\oplus}{Ar}(H)(COR)$

(3) $\overset{\oplus}{Ar}(H)(COR) + AlCl_4^- \longrightarrow Ar{-}\underset{\underset{O}{\|}}{C}{-}R + HCl + AlCl_3$

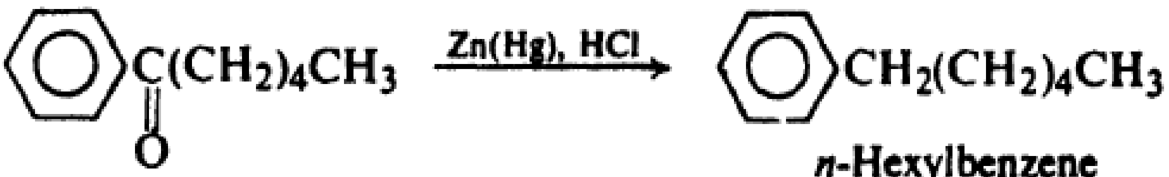
In planning the synthesis of diaryl ketones, ArCOAr′, it is particularly important to select the right combination of ArCOCl and Ar′H. In the preparation of *m*-nitrobenzophenone, for example, the nitro group can be present in the acid chloride but not in the ring undergoing substitution, since as a strongly deactivating group it prevents the Friedel-Crafts reaction (Sec. 12.8).


O$_2$N
m-Nitrobenzophenone
AlCl$_3$
Benzene
O$_2$N
COCl
m-Nitrobenzoyl chloride
PCl$_5$
O$_2$N
COOH
m-Nitrobenzoic acid
HNO$_3$, H$_2$SO$_4$
CH$_3$
Toluene
KMnO$_4$
COOH
Benzoic acid


No reaction
AlCl$_3$
O$_2$N
+
COCl
Nitrobenzene
Benzoyl chloride

Friedel-Crafts acylation is one of the most important methods of preparing ketones in which the carbonyl group is attached to an aromatic ring. Once formed, these ketones may be converted into secondary alcohols by reduction, into tertiary alcohols by reaction with Grignard reagents, and into many other important classes of compounds, as we shall see.

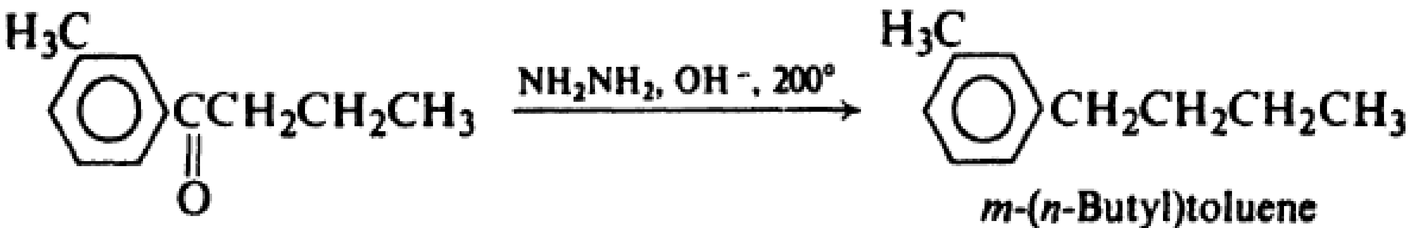
Of particular importance is the conversion of the acyl group into an alkyl group. This can be accomplished by the **Clemmensen reduction** (amalgamated zinc and concentrated hydrochloric acid), or the **Wolff-Kishner reduction** (hydrazine and base). For example:



n-Pentyl phenyl ketone

n-Hexylbenzene

Clemmensen reduction



n-Propyl *m*-tolyl ketone

m-(*n*-Butyl)toluene

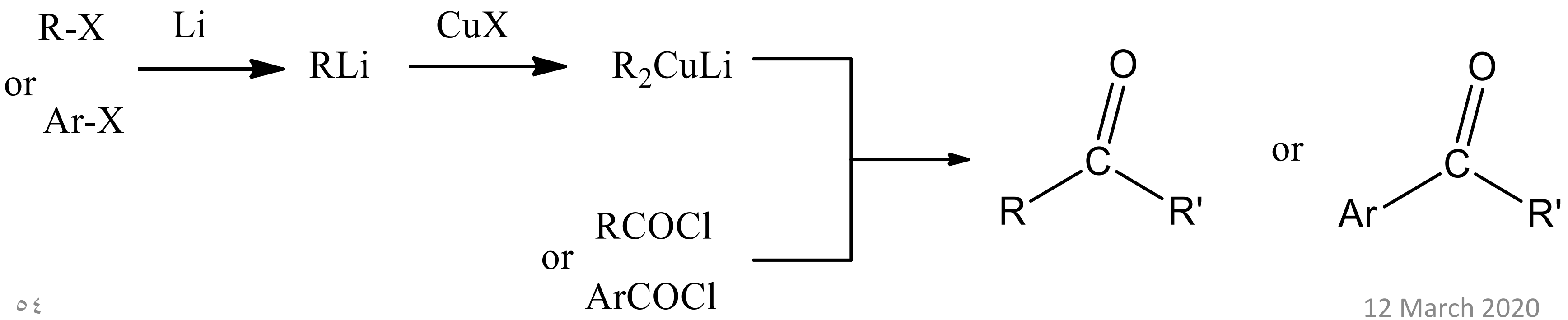
Wolff-Kishner reduction

3- Preparation of ketones by use of Organocopper Compounds:

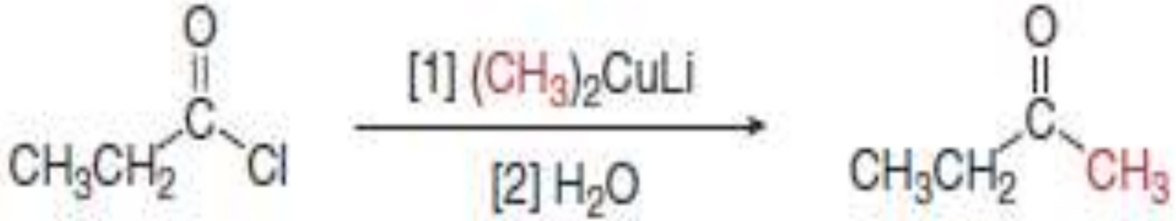
The reaction Alkyl or Aryl halides with lithium gives lithium compounds, Which on reaction with copper halides give

Lithium dialkyl cuprate,(less reactive)

The reaction of the later with acid chlorides give the corresponding Ketones:

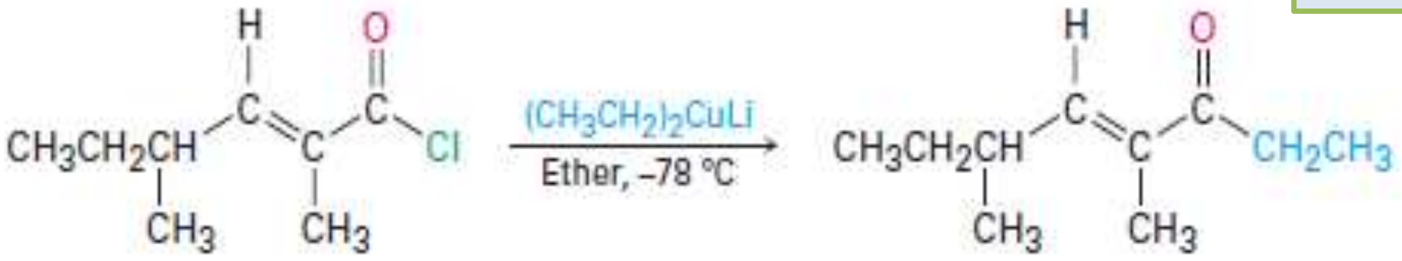


Example



★ The reaction is generally carried out at −78 °C in ether solution, and yields are often excellent. For example, manicone, a substance secreted by male ants to coordinate ant pairing and mating, has been synthesized by reaction of lithium diethylcopper with (*E*)-2,4-dimethyl-2-hexenoyl chloride.

Formone

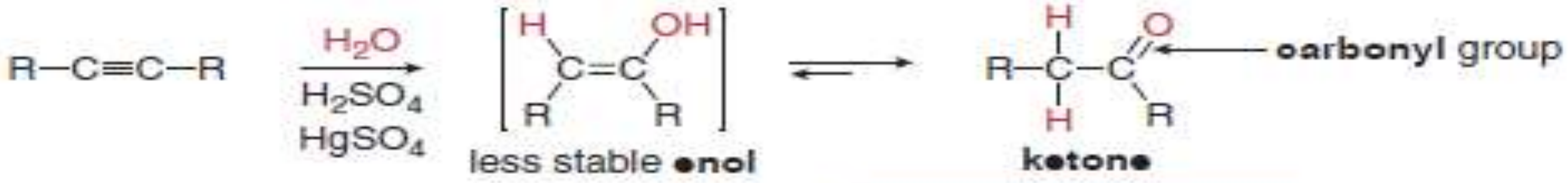


2,4-Dimethyl-2-hexenoyl chloride

4,6-Dimethyl-4-octen-3-one (manicone, 92%)

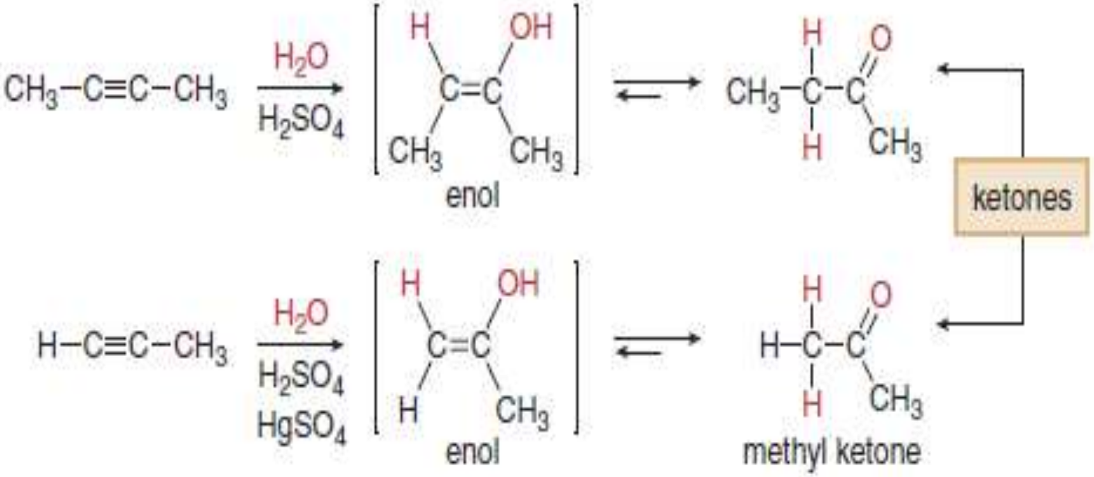
★ Note that the diorganocopper reaction occurs only with acid chlorides. Carboxylic acids, esters, acid anhydrides, and amides do not react with lithium diorganocopper reagents.

4- Addition of water to Acetylenes:



H$_2$O has been added.

Examples



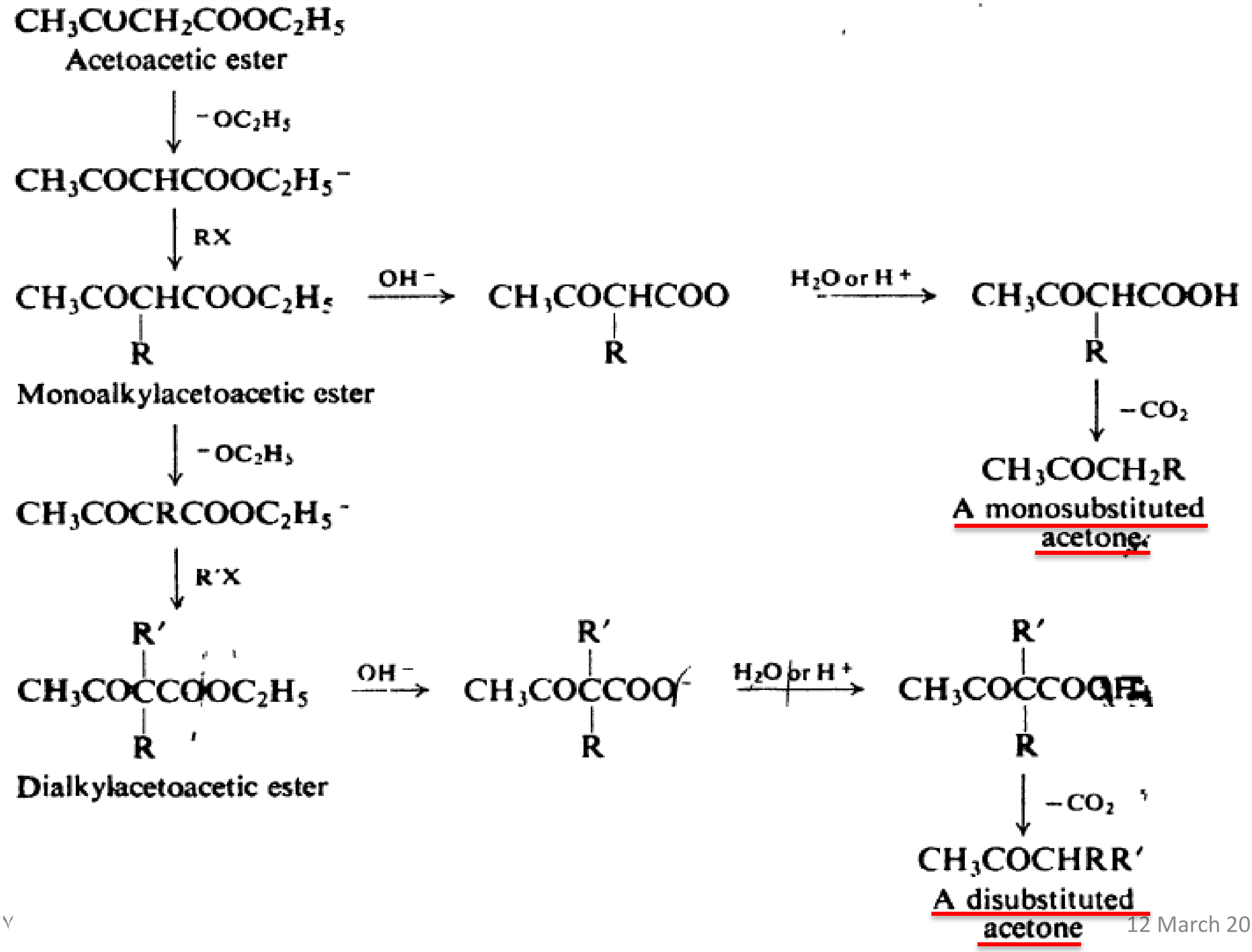
Markovnikov addition of H_2O

H adds to the terminal C.

Because an enol contains both a C=C and a hydroxy group, the name **enol** comes from **alkene** + **alcohol**.

HgSO$_4$ is often used in the hydration of internal alkynes as well, because hydration can be carried out under milder reaction conditions.

5- Acetoacetic ester synthesis of Ketones:



$CH_3COCH_2COOC_2H_5$

Acetoacetic ester

$$\xrightarrow{^-OC_2H_5} CH_3COCHCOOC_2H_5^- \xrightarrow{RX} CH_3CO\underset{R}{CH}COOC_2H_5$$

Monoalkylacetoacetic ester

$$CH_3CO\underset{R}{CH}COOC_2H_5 \xrightarrow{OH^-} CH_3CO\underset{R}{CH}COO \xrightarrow{H_2O\text{ or }H^+} CH_3CO\underset{R}{CH}COOH \xrightarrow{-CO_2} CH_3COCH_2R$$

A monosubstituted acetone

$$CH_3CO\underset{R}{CH}COOC_2H_5 \xrightarrow{^-OC_2H_5} CH_3COCRCOOC_2H_5^- \xrightarrow{R'X} CH_3CO\overset{R'}{\underset{R}{C}}COOC_2H_5$$

Dialkylacetoacetic ester

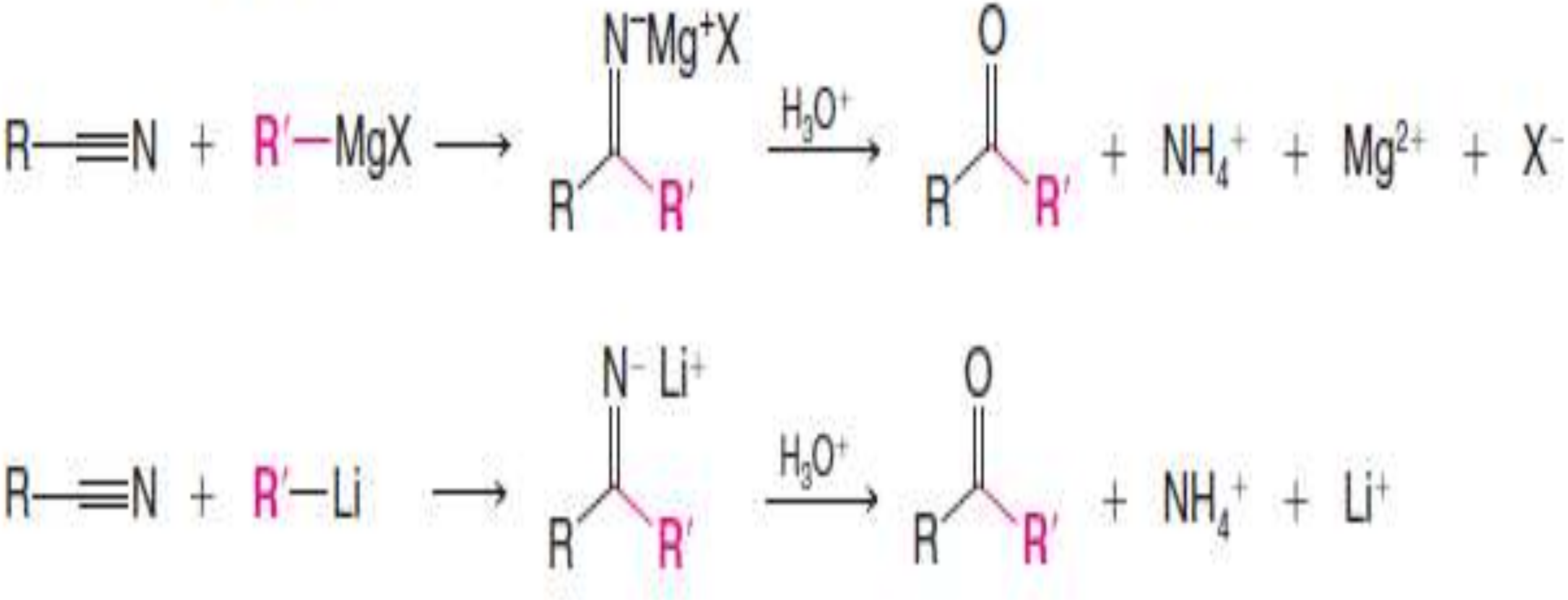
$$CH_3CO\overset{R'}{\underset{R}{C}}COOC_2H_5 \xrightarrow{OH^-} CH_3CO\overset{R'}{\underset{R}{C}}COO^- \xrightarrow{H_2O\text{ or }H^+} CH_3CO\overset{R'}{\underset{R}{C}}COOH \xrightarrow{-CO_2} CH_3COCHRR'$$

A disubstituted acetone

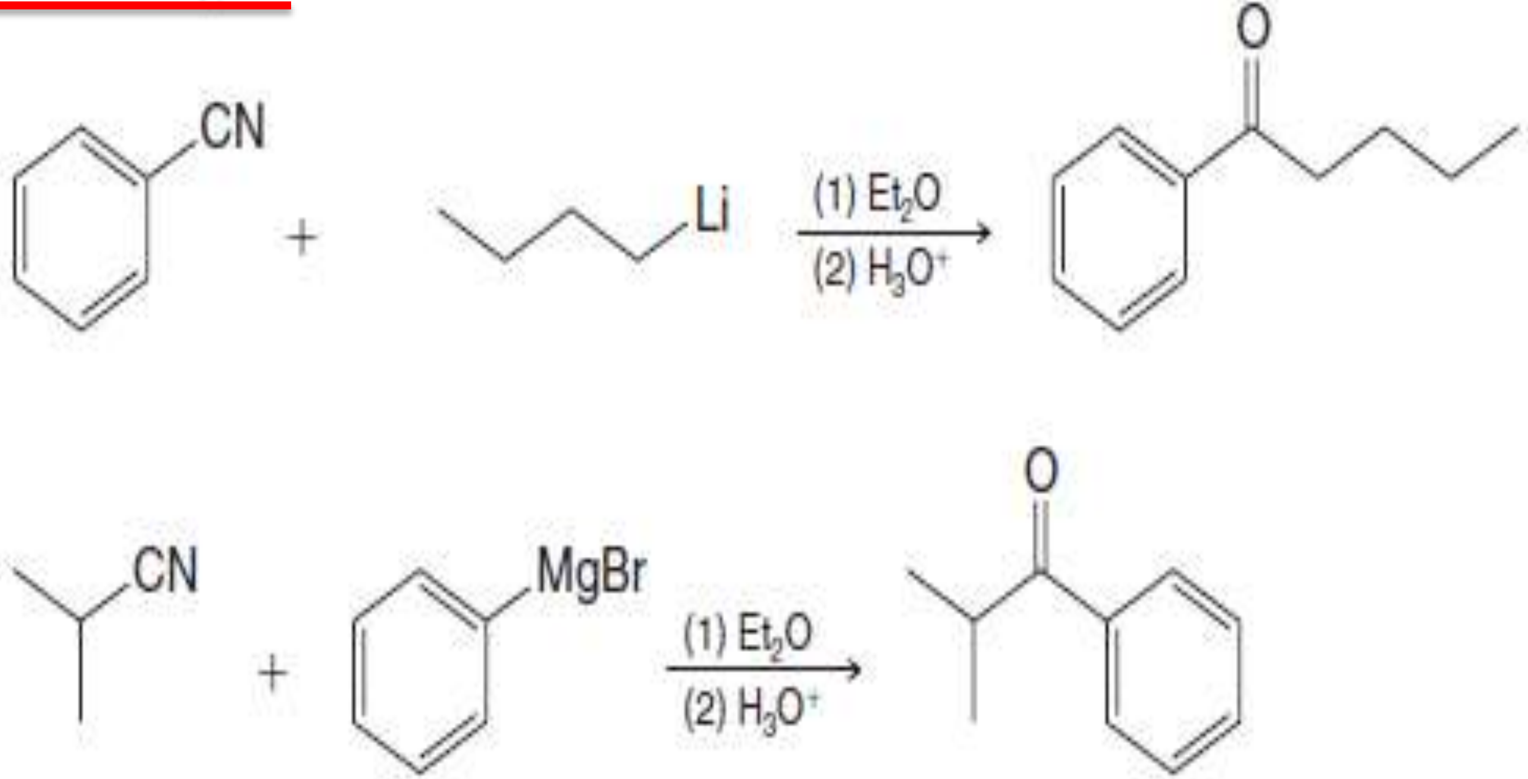
6- Ketones from Nitriles:

Treating a nitrile (R—C≡N) with either a Grignard reagent or an organolithium reagent followed by hydrolysis yields a ketone.

General Reactions



Specific Examples



2-Cyanopropane

2-Methyl-1-phenylpropanone
(isopropyl phenyl ketone)