First class

Chemical Engineering
Second Semester
Organic Chemistry

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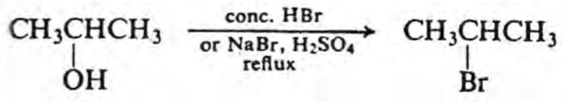
— كورس - عمليات —

Reactivity of HX: HI > HBr > HCl

Reactivity of ROH: allyl, benzyl > 3° > 2° > 1°

Examples:

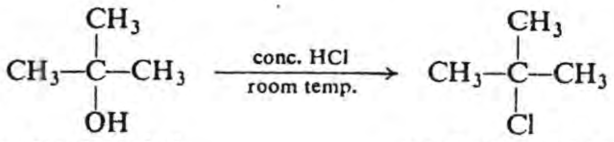


$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3} \xrightarrow[\text{or NaBr, }H_2SO_4\text{, reflux}]{\text{conc. HBr}} \underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3}$$

Isopropyl alcohol → Isopropyl bromide

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{HCl,\ ZnCl_2} CH_3CH_2CH_2CH_2CH_2Cl$$

n-Pentyl alcohol → *n*-Pentyl chloride



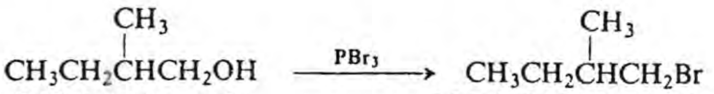
$$CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{room temp.}]{\text{conc. HCl}} CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

tert-Butyl alcohol → *tert*-Butyl chloride

2. Reaction with phosphorus trihalides. Discussed in Sec. 16.10.

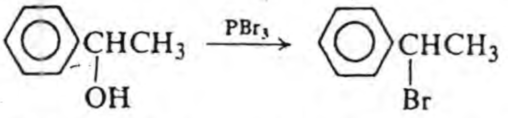
$$R{-}OH + PX_3 \longrightarrow RX + H_3PO_3$$
$$(PX_3 = PBr_3,\ PI_3)$$

Examples:



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH \xrightarrow{PBr_3} CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Br$$

2-Methyl-1-butanol → 2-Methyl-1-bromobutane

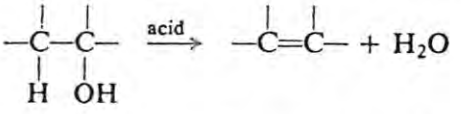


1-Phenylethanol → 1-Bromo-1-phenylethane

$$CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I$$

Ethyl alcohol → Ethyl iodide

3. Dehydration. Discussed in Secs. 5.19–5.23, and 16.3.



$$-\underset{\underset{\displaystyle H}{|}}{\overset{|}{C}}-\underset{\underset{\displaystyle OH}{|}}{\overset{|}{C}}- \xrightarrow{\text{acid}} -\overset{|}{C}{=}\overset{|}{C}- + H_2O$$

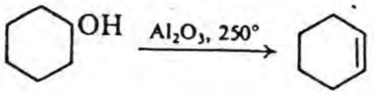
Rearrangement may occur

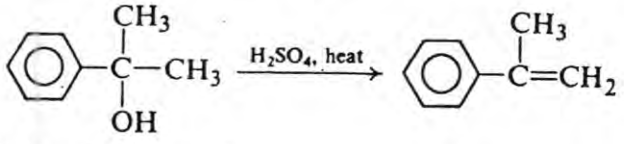
Reactivity of ROH: 3° > 2° > 1°

Examples:

$$CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4,\ \text{heat}} CH_3CH{=}CHCH_3 \text{ and } CH_3CH_2CH{=}CH_2$$

n-Butyl alcohol → 2-Butene (*Major product*) and 1-Butene





2-Phenyl-2-propanol 2-Phenylpropene

O---H BOND CLEAVAGE

$$\mathrm{RO}\vdots\mathrm{H}$$

4. **Reaction as acids: reaction with active metals.** Discussed in Sec. 16.6.

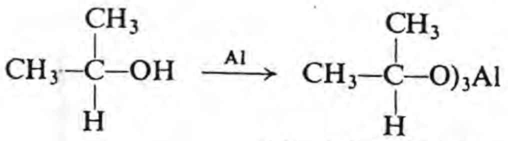
$$RO{-}H + M \longrightarrow RO^-M^+ + \tfrac{1}{2}H_2 \qquad M = Na,\ K,\ Mg,\ Al,\ etc.$$

Reactivity of ROH: $CH_3OH > 1° > 2° > 3°$

Examples:

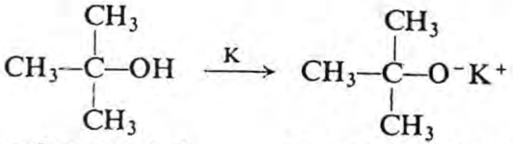
$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^-Na^+ + \tfrac{1}{2}H_2$$

Sodium ethoxide



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \xrightarrow{Al} (CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O)_3Al$$

Aluminium isopropoxide

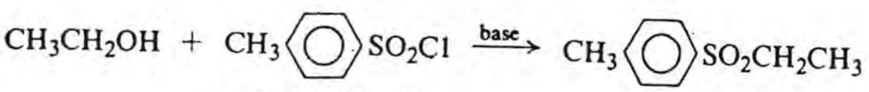


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow{K} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O^-K^+$$

tert-Butyl alcohol Potassium *tert*-butoxide

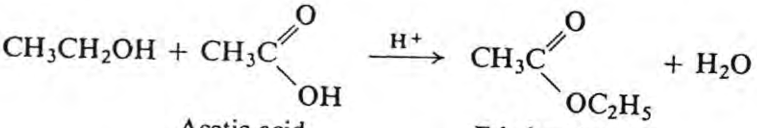
5. **Ester formation.** Discussed in Secs. 16.7 and 18.16.

Examples:



Tosyl chloride
(*p*-Toluenesulfonyl chloride)

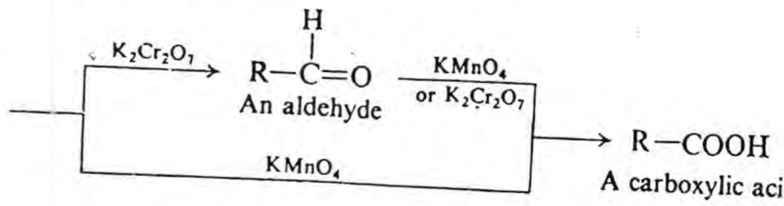
Ethyl tosylate



Acetic acid Ethyl acetate

6. **Oxidation.** Discussed in Sec. 16.8.

Primary: R—CH$_2$OH

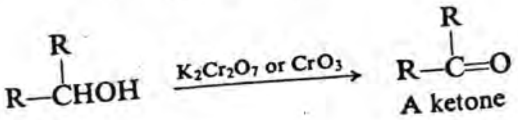


An aldehyde

A carboxylic acid

DEHYDRATION

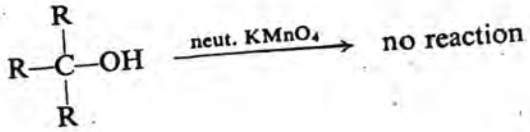
Secondary:



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

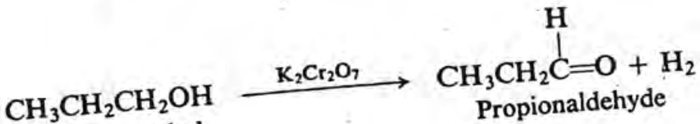
A ketone

Tertiary:



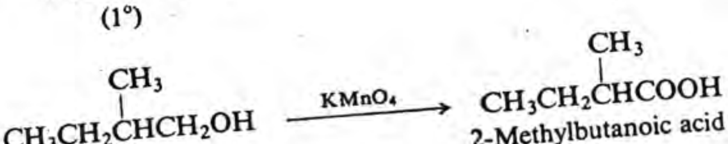
$$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OH \xrightarrow{\text{neut. } KMnO_4} \text{no reaction}$$

Examples:



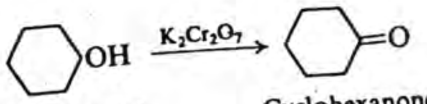
$$CH_3CH_2CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3CH_2\overset{H}{\overset{|}{C}}=O + H_2$$

n-Propyl alcohol (1°) → Propionaldehyde

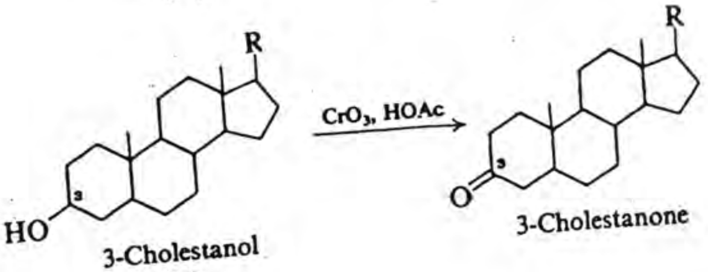


$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{KMnO_4} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCOOH$$

2-Methyl-1-butanol (1°) → 2-Methylbutanoic acid



Cyclohexanol (2°) → Cyclohexanone



3-Cholestanol (2°) → 3-Cholestanone

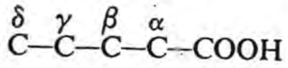
[redacted]

—Carboxylic acids—

[redacted]

and *caproic*, *caprylic*, and *capric acids* are all found in goat fat (Latin: *caper*, goat).

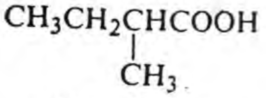
Branched-chain acids and substituted acids are named as derivatives of the straight-chain acids. To indicate the position of attachment, the Greek letters, α-, β-, γ-, δ-, etc., are used; the α-carbon is the one bearing the carboxyl group.



$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-COOH$$

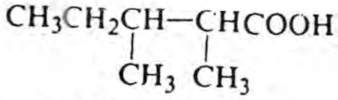
Used in common names

For example:



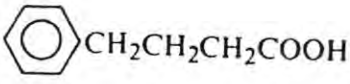
$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCOOH$$

α-Methylbutyric acid

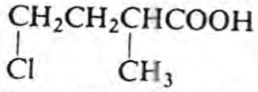


$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}HCOOH$$

α,β-Dimethylvaleric acid

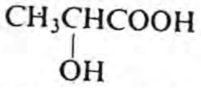


γ-Phenylbutyric acid



$$\underset{Cl}{\underset{|}{C}}H_2CH_2\underset{CH_3}{\underset{|}{C}}HCOOH$$

γ-Chloro-α-methylbutyric acid



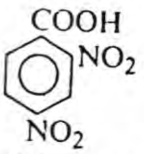
$$CH_3\underset{OH}{\underset{|}{C}}HCOOH$$

α-Hydroxypropionic acid
Lactic acid

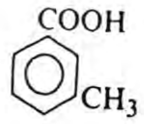
Generally the parent acid is taken as the one of longest carbon chain, although some compounds are named as derivatives of acetic acid.

Aromatic acids, ArCOOH, are usually named as derivatives of the parent acid, **benzoic acid**, C_6H_5COOH. The methylbenzoic acids are given the special name of *toluic acids.*

p-Bromobenzoic acid



2,4-Dinitrobenzoic acid

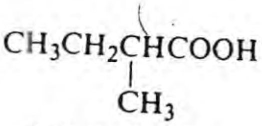


m-Toluic acid

The **IUPAC names** follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the *-e* of the corresponding alkane with **-oic acid**. For example:

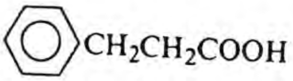
$CH_3CH_2CH_2CH_2COOH$

Pentanoic acid

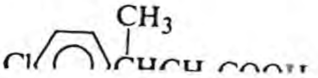


$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCOOH$$

2-Methylbutanoic acid



3-Phenylpropanoic acid

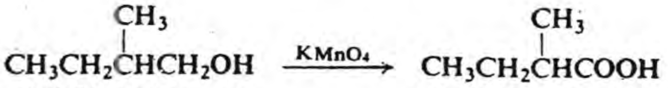


PREPARATION OF CARBOXYLIC ACIDS

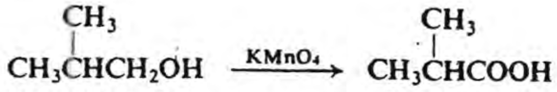
1. Oxidation of primary alcohols. Discussed in Sec. 16.8.

$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

Examples:



$$\underset{\text{2-Methyl-1-butanol}}{CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH} \xrightarrow{KMnO_4} \underset{\text{2-Methylbutanoic acid}}{CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCOOH}$$

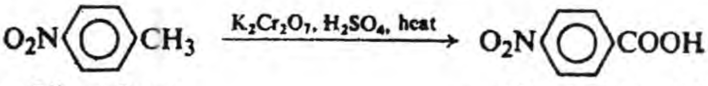


$$\underset{\text{Isobutyl alcohol}}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH} \xrightarrow{KMnO_4} \underset{\text{Isobutyric acid}}{CH_3\overset{CH_3}{\overset{|}{C}}HCOOH}$$

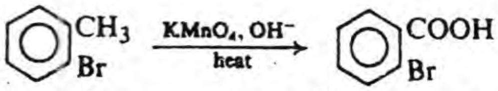
2. Oxidation of alkylbenzenes. Discussed in Sec. 12.10.

$$Ar{-}R \xrightarrow[K_2C_2O_7]{KMnO_4 \text{ or } K_2Cr_2O_7} Ar{-}COOH$$

Examples:



p-Nitrotoluene *p*-Nitrobenzoic acid

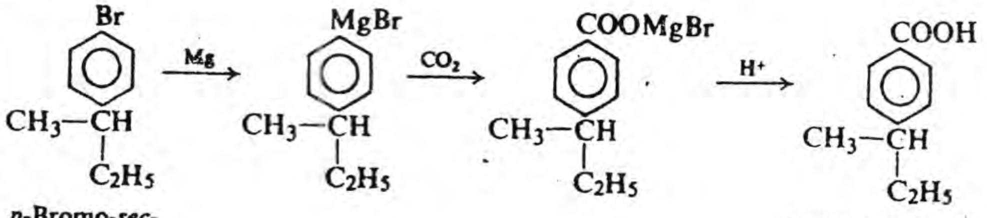


o-Bromotoluene *o*-Bromobenzoic acid

3. Carbonation of Grignard reagents. Discussed in Sec. 18.7.

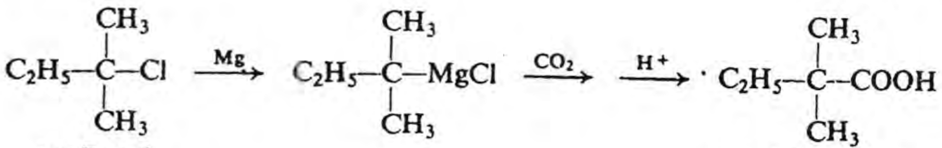
$$\underset{\text{(or ArX)}}{RX} \xrightarrow{Mg} RMgX \xrightarrow{CO_2} RCOOMgX \xrightarrow{H^+} \underset{\text{(or ArCOOH)}}{RCOOH}$$

Examples:



p-Bromo-*sec*-butylbenzene

p-*sec*-Butylbenzoic acid



$$\underset{\substack{tert\text{-Pentyl}\\ \text{chloride}}}{C_2H_5{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}Cl} \xrightarrow{Mg} C_2H_5{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}MgCl \xrightarrow{CO_2} \xrightarrow{H^+} \underset{\substack{\text{Ethyldimethylacetic}\\ \text{acid}\\ \text{(2,2-Dimethylbutanoic}\\ \text{acid)}}}{C_2H_5{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}COOH}$$

4. Hydrolysis of nitriles. Discussed in Sec. 18.8.

$$\begin{array}{c} R{-}C{\equiv}N \\ \text{or} \\ Ar{-}C{\equiv}N \end{array} + H_2O \xrightarrow{\text{acid or base}} \begin{array}{c} R{-}COOH \\ \text{or} \\ Ar{-}COOH \end{array} + NH_3$$

The rest of the molecule undergoes reactions characteristic of its structure; it may be aliphatic or aromatic, saturated or unsaturated, and may contain a variety of other functional groups.

REACTIONS OF CARBOXYLIC ACIDS

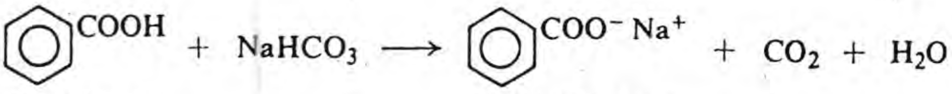
1. Acidity. Salt formation. Discussed in Secs. 18.4, 18.10–18.14.

$$RCOOH \rightleftarrows RCOO^- + H^+$$

Examples:

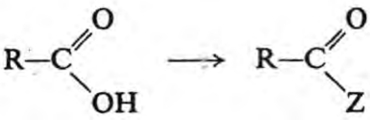
$$\underset{\text{Acetic acid}}{2CH_3COOH} + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3COO^-)_2Zn^{++}} + H_2$$

$$\underset{\text{Lauric acid}}{CH_3(CH_2)_{10}COOH} + NaOH \longrightarrow \underset{\text{Sodium laurate}}{CH_3(CH_2)_{10}COO^-Na^+} + H_2O$$



Benzoic acid Sodium benzoate

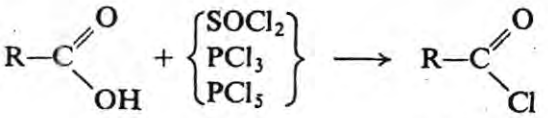
2. Conversion into functional derivatives



$$R{-}COOH \longrightarrow R{-}COZ$$

(Z = —Cl, —OR′, —NH$_2$)

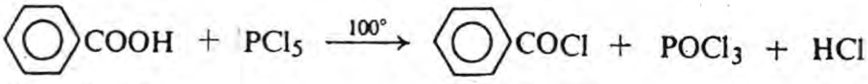
(a) Conversion into acid chlorides. Discussed in Sec. 18.15.



$$R{-}COOH + \begin{Bmatrix} SOCl_2 \\ PCl_3 \\ PCl_5 \end{Bmatrix} \longrightarrow R{-}COCl$$

Acid chloride

Examples:

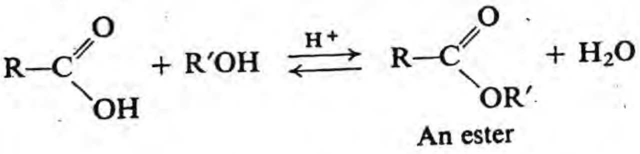


Benzoic acid Benzoyl chloride

$$\underset{\text{Stearic acid}}{n\text{-}C_{17}H_{35}COOH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{reflux}} \underset{\text{Stearoyl chloride}}{n\text{-}C_{17}H_{35}COCl} + SO_2 + HCl$$

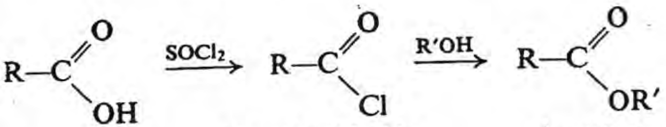
$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \xrightarrow{50^\circ} \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

(b) **Conversion into esters.** Discussed in Secs. 18.16 and 20.15.



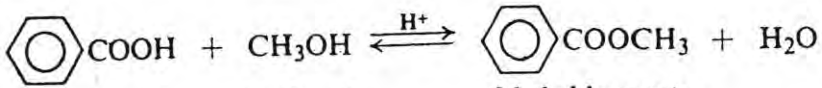
An ester

Reactivity of R'OH: 1°> 2° (> 3°)

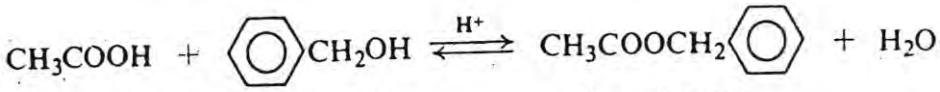


An acid chloride An ester

Examples:



Benzoic acid Methanol Methyl benzoate

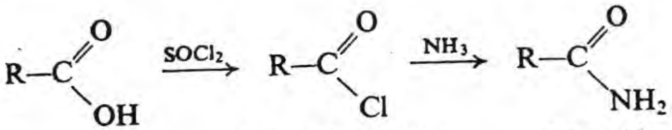


Acetic acid Benzyl alcohol Benzyl acetate

$$(CH_3)_3CCOOH \xrightarrow{SOCl_2} (CH_3)_3CCOCl \xrightarrow{C_2H_5OH} (CH_3)_3CCOOC_2H_5$$

Trimethylacetic acid Ethyl trimethylacetate

(c) **Conversion into amides.** Discussed in Sec. 18.17.



An acid chloride An amide

Example:

$$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow{NH_3} C_6H_5CH_2CONH_2$$

Phenylacetic acid Phenylacetyl chloride Phenylacetamide

3. **Reduction.** Discussed in Sec. 18.18.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

1° alcohol

Also reduced via esters (Sec. 20.22)

Examples:

$$4(CH_3)_3CCOOH + 3LiAlH_4 \xrightarrow{ether} [(CH_3)_3CCH_2O]_4AlLi + 2LiAlO_2 + 4H_2 \xrightarrow{H^+} (CH_3)_3CCH_2OH$$

Trimethylacetic acid

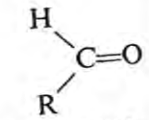
Neopentyl alcohol (2,2-Dimethyl-1-propanol)

Aldehydes and Ketones

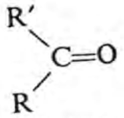
Nucleophilic Addition

[redacted] Structure

Aldehydes are compounds of the general formula RCHO; ketones are compounds of the general formula RR′CO. The groups R and R′ may be aliphatic or aromatic.



An aldehyde

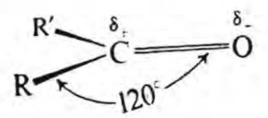


A ketone

Both aldehydes and ketones contain the carbonyl group, C=O, and are often referred to collectively as **carbonyl compounds**. *It is the carbonyl group that largely determines the chemistry of aldehydes and ketones.*

It is not surprising to find that aldehydes and ketones resemble each other closely in most of their properties. However, there is a hydrogen atom attached to the carbonyl group of aldehydes, and there are two organic groups attached to the carbonyl group of ketones. This difference in structure affects their properties in two ways: (a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty; (b) aldehydes are usually more reactive than ketones toward nucleophilic addition, the characteristic reaction of carbonyl compounds.

Let us examine the structure of the carbonyl group. Carbonyl carbon is joined to three other atoms by σ bonds; since these bonds utilize sp^2 orbitals (Sec. 1.10), they lie in a plane, and are 120° apart. The remaining p orbital of the carbon overlaps a p orbital of oxygen to form a π bond; carbon and oxygen are thus



joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon is *flat*; oxygen, carbonyl carbon, and the two atoms directly attached to carbonyl carbon lie in a plane.

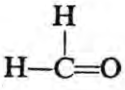
The electrons of the carbonyl double bond hold together atoms of quite different electronegativity, and hence the electrons are not equally shared; in particular, the mobile π cloud is pulled strongly toward the more electronegative atom, oxygen.

The facts are consistent with the orbital picture of the carbonyl group. Electron diffraction and spectroscopic studies of aldehydes and ketones show that carbon, oxygen, and the two other atoms attached to carbonyl carbon lie in a plane; the three bond angles of carbon are very close to 120°. The large dipole moments (2.3–2.8 D) of aldehydes and ketones indicate that the electrons of the carbonyl group are quite unequally shared. We shall see how the physical and chemical properties of aldehydes and ketones are determined by the structure of the carbonyl group.

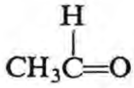
19.2 Nomenclature

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

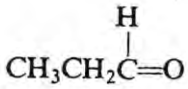
The IUPAC names of aldehydes follow the usual pattern. The longest chain carrying the —CHO group is considered the parent structure and is named by replacing the *-e* of the corresponding alkane by *-al.* The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-1. Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to *alpha* of the common name.


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

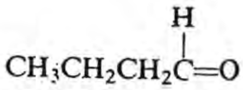
Formaldehyde
Methanal


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

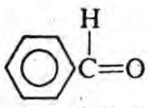
Acetaldehyde
Ethanal

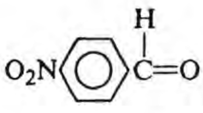

$CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}=O$

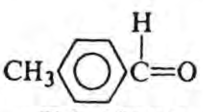
Propionaldehyde
Propanal

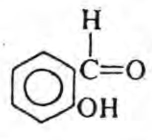

$CH_3CH_2CH_2\overset{\overset{\displaystyle H}{|}}{C}=O$

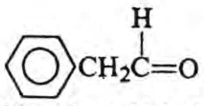
n-Butyraldehyde
Butanal

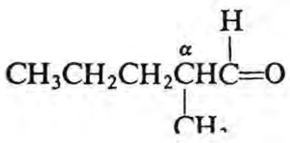

Benzaldehyde

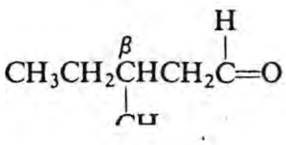

p-Nitrobenzaldehyde

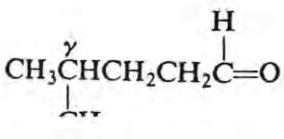

p-Tolualdehyde


Salicylaldehyde
(*o*-Hydroxybenzaldehyde)


Phenylacetaldehyde
(Phenylethanal)

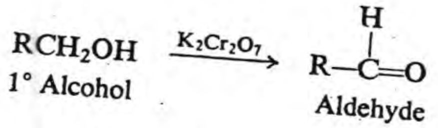

$CH_3CH_2CH_2\underset{|}{\overset{\alpha}{C}}H\overset{\overset{\displaystyle H}{|}}{C}=O$


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


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

PREPARATION OF ALDEHYDES

1. Oxidation of primary alcohols. Discussed in Secs. 16.8 and 19.5.

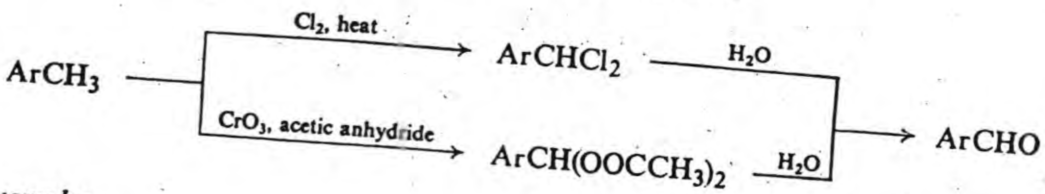


$$RCH_2OH \xrightarrow{K_2Cr_2O_7} R{-}\overset{H}{\overset{|}{C}}{=}O$$

Example:

$$\underset{\substack{n\text{-Butyl alcohol}\\ \text{(1-Butanol)}\\ B.p.\ 118°}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{K_2Cr_2O_7,\ H_2SO_4,\ \text{warm}} \underset{\substack{n\text{-Butyraldehyde}\\ \text{(Butanal)}\\ B.p.\ 76°}}{CH_3CH_2CH_2CHO}$$

2. Oxidation of methylbenzenes. Discussed in Sec. 19.5.



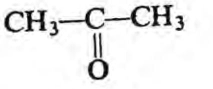
Examples:

p-Bromotoluene

p-Bromobenzaldehyde

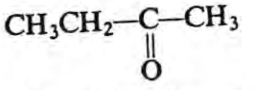
The simplest aliphatic ketone has the common name of *acetone*. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word *ketone*. A ketone in which the carbonyl group is attached to a benzene ring is named as a *–phenone*, as illustrated below.

According to the IUPAC system, the longest chain carrying the carbonyl group is considered the parent structure, and is named by replacing the *–e* of the corresponding alkane with *–one*. The positions of various groups are indicated by numbers, the carbonyl carbon being given the lowest possible number.



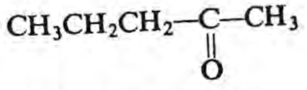
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Acetone
Propanone



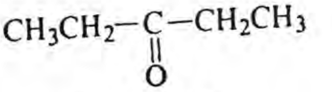
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

Methyl ethyl ketone
Butanone



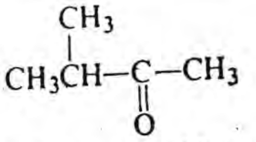
$CH_3CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

Methyl *n*-propyl ketone
2-Pentanone



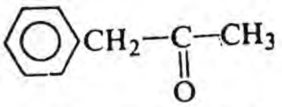
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

Ethyl ketone
3-Pentanone

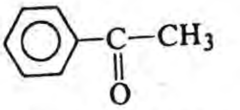


$CH_3\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{O}{\|}}{C}-CH_3$

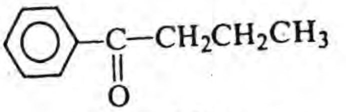
Methyl isopropyl ketone
3-Methyl-2-butanone



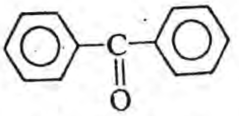
Benzyl methyl ketone
1-Phenyl-2-propanone



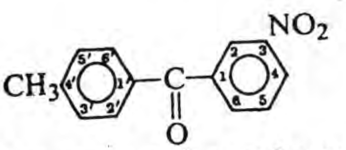
Acetophenone



n-Butyrophenone



Benzophenone

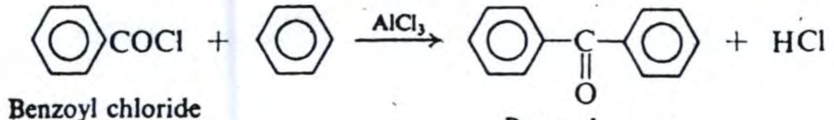


3-Nitro-4′-methylbenzophenone

19.3 Physical properties

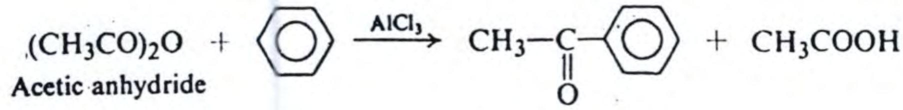
The polar carbonyl group makes aldehydes and ketones polar compounds, and hence they have higher boiling points than non-polar compounds of comparable molecular weight. By themselves, they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids. For example, compare *n*-butyraldehyde (b.p. 76°) and methyl ethyl ketone (b.p. 80°) with *n*-pentane (b.p. 36°) and ethyl ether (b.p. 35°) on the one hand, and with *n*-butyl alcohol (b.p. 118°) and propionic acid (b.p. 141°) on the other.

The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons. Aldehydes and ketones are soluble in



Benzoyl chloride

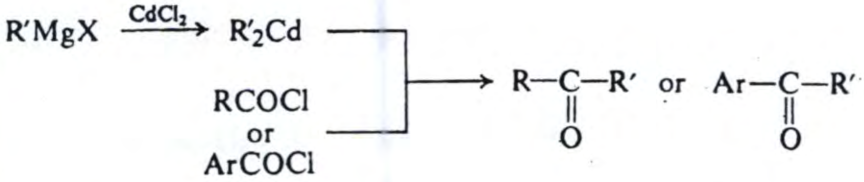
Benzophenone
(Phenyl ketone)



Acetic anhydride

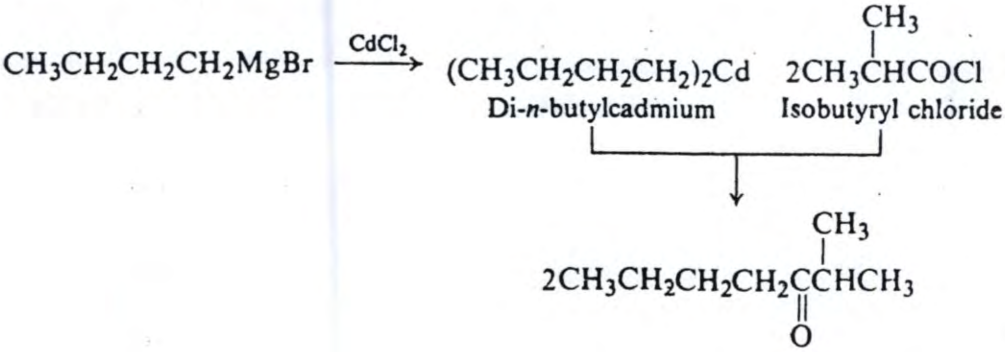
Acetophenone
(Methyl phenyl ketone)

3. **Reaction of acid chlorides with organocadmium compounds.** Discussed in Sec. 19.7.



R′ *must be aryl or primary alkyl*

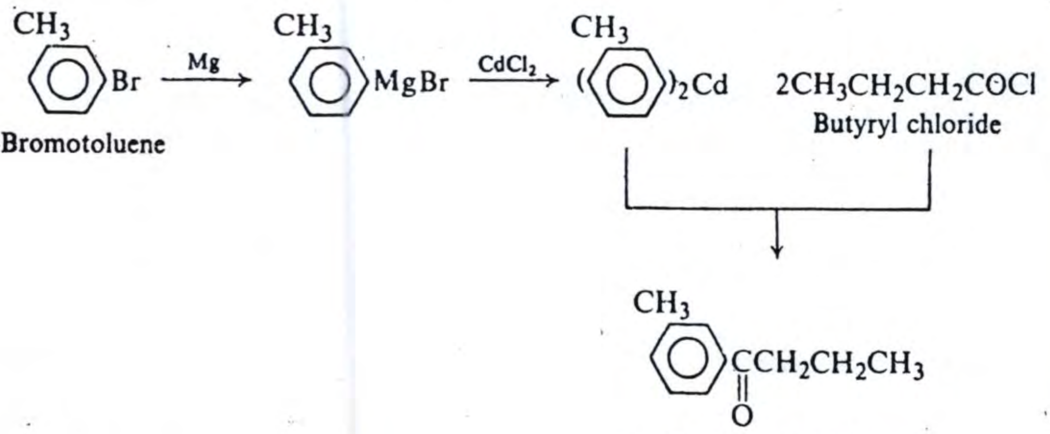
Examples:



Di-*n*-butylcadmium

Isobutyryl chloride

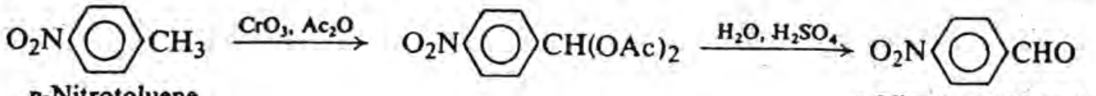
n-Butyl isopropyl ketone
(2-Methyl-3-heptanone)



m-Bromotoluene

Butyryl chloride

n-Propyl *m*-tolyl ketone



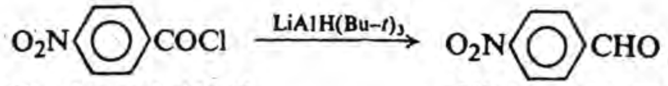
p-Nitrotoluene

p-Nitrobenzaldehyde

3. Reduction of acid chlorides. Discussed in Sec. 19.4.

$$\underset{\text{Acid chloride}}{\text{RCOCl or ArCOCl}} \xrightarrow{\text{LiAlH(Bu-}t)_3} \underset{\text{Aldehyde}}{\text{RCHO or ArCHO}}$$

Examples:



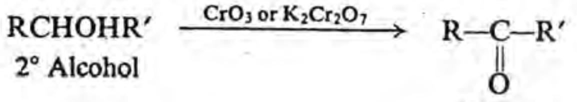
p-Nitrobenzoyl chloride

p-Nitrobenzaldehyde

4. Reimer-Tiemann reaction. Phenolic aldehydes. Discussed in Sec. 24.12.

PREPARATION OF KETONES

1. Oxidation of secondary alcohols. Discussed in Sec. 16.8.

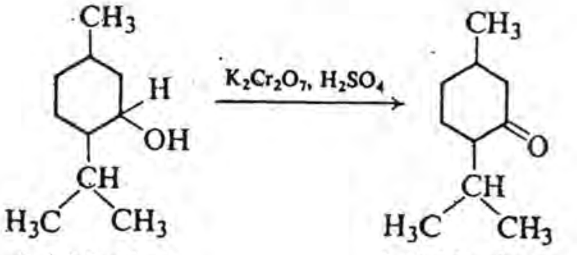


$$\underset{2^\circ\text{ Alcohol}}{\text{RCHOHR}'} \xrightarrow{\text{CrO}_3\text{ or K}_2\text{Cr}_2\text{O}_7} \text{R}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{R}'$$

2° Alcohol

Ketone

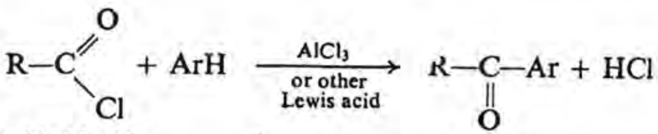
Example:



(−)-Menthol

(−)-Menthone

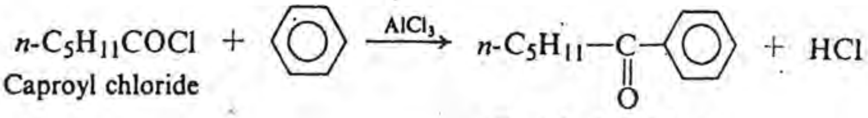
2. Friedel-Crafts acylation. Discussed in Sec. 19.6.



Acid chloride

Ketone

Examples:



Caproyl chloride

n-Pentyl phenyl ketone

No rearrangement of n-pentyl group

REACTIONS OF ALDEHYDES AND KETONES

1. Oxidation. Discussed in Sec. 19.9.

(a) Aldehydes

$$\mathrm{RCHO\ or\ ArCHO} \xrightarrow[\mathrm{K_2Cr_2O_7}]{\mathrm{Ag(NH_3)_2{}^+},\ \mathrm{KMnO_4}} \mathrm{RCOOH\ or\ ArCOOH}$$

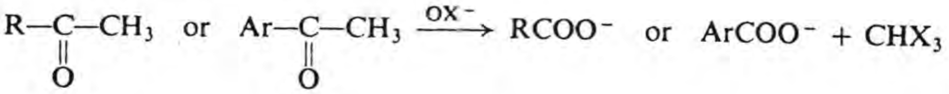
Used chiefly for detection of aldehydes

Examples:

$$\mathrm{CH_3CHO + 2Ag(NH_3)_2{}^+ + 3OH^- \longrightarrow 2Ag + CH_3COO^- + 4NH_3 + 2H_2O}$$

Colorless solution *Silver mirror* *Tollens' test*

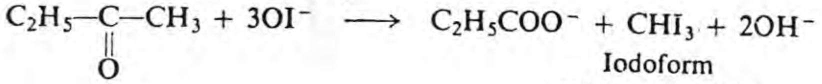
(b) Methyl ketones



$$\mathrm{R{-}\underset{\substack{\|\\O}}{C}{-}CH_3\ or\ Ar{-}\underset{\substack{\|\\O}}{C}{-}CH_3 \xrightarrow{OX^-} RCOO^-\ or\ ArCOO^- + CHX_3}$$

Haloform reaction

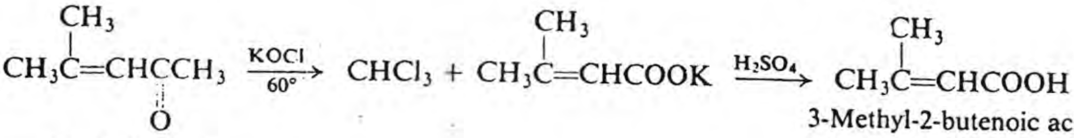
Examples:



$$\mathrm{C_2H_5{-}\underset{\substack{\|\\O}}{C}{-}CH_3 + 3OI^- \longrightarrow C_2H_5COO^- + CHI_3 + 2OH^-}$$

Iodoform

Yellow; m.p. 119°

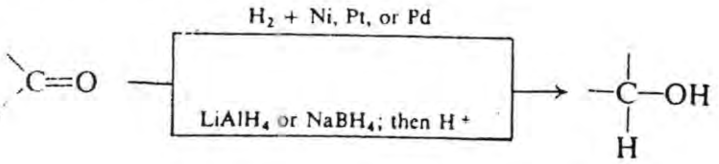


$$\mathrm{CH_3\overset{CH_3}{\overset{|}{C}}{=}CH\underset{\substack{\|\\O}}{C}CH_3 \xrightarrow[60^\circ]{KOCl} CHCl_3 + CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCOOK \xrightarrow{H_2SO_4} CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCOOH}$$

Mesityl oxide (4-Methyl-3-penten-2-one) 3-Methyl-2-butenoic acid

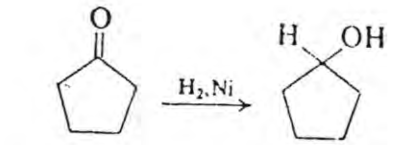
2. Reduction

(a) Reduction to alcohols. Discussed in Sec. 19.10.

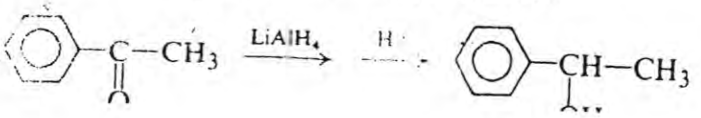


$$\mathrm{{>}C{=}O} \xrightarrow[\mathrm{LiAlH_4\ or\ NaBH_4;\ then\ H^+}]{\mathrm{H_2 + Ni,\ Pt,\ or\ Pd}} \mathrm{{-}\underset{\substack{|\\H}}{\overset{|}{C}}{-}OH}$$

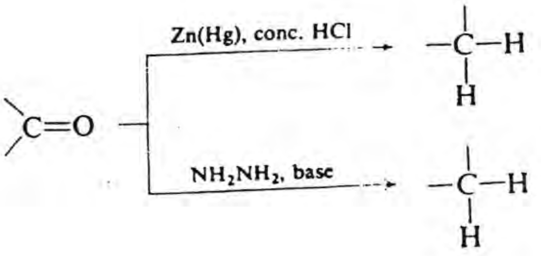
Examples:



Cyclopentanone Cyclopentanol



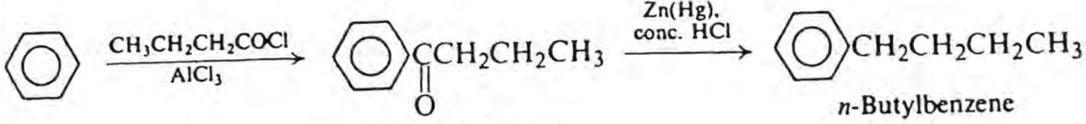
(b) Reduction to hydrocarbons. Discussed in Sec. 19.10.



Clemmensen reduction
for compounds sensitive to base

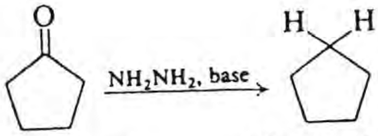
Wolff-Kishner reduction
for compounds sensitive to acid

Examples:



n-Butyrophenone
(Phenyl n-propyl ketone)

n-Butylbenzene

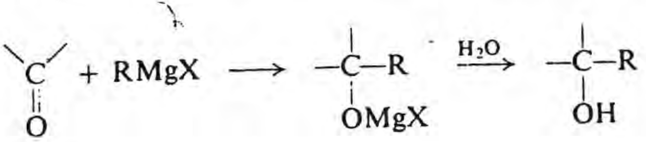


Cyclopentanone

Cyclopentane

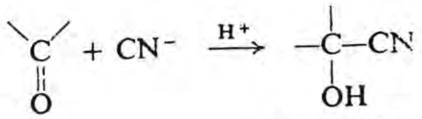
(c) Reductive amination. Discussed in Sec. 22.11.

3. Addition of Grignard reagents. Discussed in Secs. 15.12–15.15 and 19.11.



$$\overset{\diagdown\ \diagup}{\underset{\underset{O}{\|}}{C}} + RMgX \longrightarrow -\overset{|}{\underset{\underset{OMgX}{|}}{C}}-R \xrightarrow{H_2O} -\overset{|}{\underset{\underset{OH}{|}}{C}}-R$$

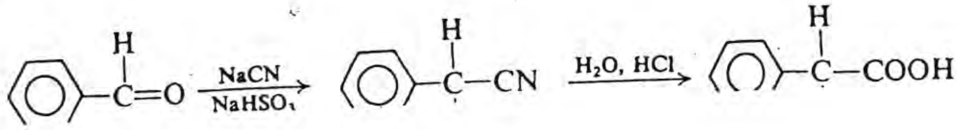
4. Addition of cyanide. Cyanohydrin formation. Discussed in Sec. 19.12.



$$\overset{\diagdown\ \diagup}{\underset{\underset{O}{\|}}{C}} + CN^- \xrightarrow{H^+} -\overset{|}{\underset{\underset{OH}{|}}{C}}-CN$$

Cyanohydrin

Examples:



Carbohydrates:-

Importance:-

Carbohydrates are widely distributed in both plant and animal tissues. They are indispensable for living organisms and serve as skeletal structures in plants and also in insects. They occur as food reserves in the storage organs of plants and animals. They are important source of energy required for the various metabolic activities of the living organisms.

In living organisms carbohydrates:-

1. Providing Energy through oxidation
2. Providing carbon for synthesis of cell component.
3. Serve as a stored form of chemical energy.

Defenition:- Carbohydrates are defined as polyhydroxy aldehyde or ketones and are generally classified as follows $C_n(H_2O)_n$ or $C_6H_{12}O_6$

Classification:- Carbohydrates are generally classified into 4 major groups:-

1- Mono saccharide
2- Disaccharide
3- Oligo sacchari
4- Polysaccharide

Function of Carbohydrates:-

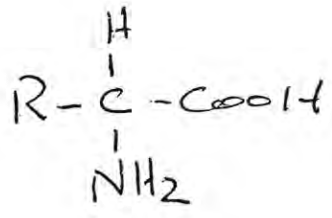
1- Source of energy.

2- Source of B- Vitamins.

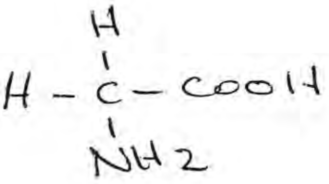
3. Role of type of carbohydrate and diabetes.

Amino Acids

Amino acids are the simplest units of a Protein molecule and they form the building blocks of Protein structure. The general formula of an amino acid can be writen as



$$R-\overset{\overset{\large H}{|}}{\underset{\underset{\large NH_2}{|}}{C}}-COOH$$



$$H-\overset{\overset{\large H}{|}}{\underset{\underset{\large NH_2}{|}}{C}}-COOH$$

Amino acid is an amino carboxylic acid. R is the Side chain and it represents The group other than $-NH_2$ and $-COOH$

Amino acid are classified into two groups according to their inclusion in the diet

1. Essential amino acid : which can not be synthesised by the living organisms.

2 Non essential amino acid :- Which can be synthesised

2/ 25

In Proteins, amino acids are linked together by linkage called Peptied bonds. It also called as the amide bond. The two amino acids joind by a Peptied bond constitute a dipeptide

Vitamins

The Vitamins are a group of complex organic compound required in small quantities by the body for the maintanance of good health. They are not normally synthesized in the body and hence they should be supplied by the diet.

Classification :-

Vitamins are generally classified into two main groups

A/ Water Soluble vitamins

B/ Fat Soluble vitamins

?/ water Soluble Vitamins:-

The members of this group are B complex vitamin and Vitamin C. They are readily soluble in water.

It consists B_1 Thiamine, Riboflavin (B_2), Niacin (B_3)

Fat soluble vitamins:-

Vitamin A, Vitamin D, Vitamin E, Vitamin K

Unlike other groups of nutrients, The Vitamins are not chemically similar to each other. Each vitamin has specific chemical structure and a specific function or functions in the living systen. Most of the Vitamins act Coenzym in the body. Normally a well_balanced diet will supply all the necessary vitamin in sufficient quantity.

Lec: 5

chemistry of Polymeric materials

Polymer Technology:-

Polymis derived from The Greak Poly and mers meaning ng many and Parts, respectively. The term Polymers, macro molecules, and gaint molecules are used to designate high molecular weight material ther natural or synthetic origin. This definition aPases ([illegible]) enormous range of materials having widely different physial, chemical, biological and

2+

Rubbers : Poly iso Prene
SBR (styrene, butadiene rubber)
Poly chloro Prene
Poly sulfide

Fibers:- Poly amide
Poly ester
Acrylic

Adhesives : are either Plastic or rubber Formulation For difinit applications

Surface Coating: Paints with solvent or dispersant
Powder coating
تحدث تفاعل كيميائي أثناء تطايره ويعطي أسطح بالطلاء (مثل الإيبوكسي : Convertible
طلاء أظافر Lacquers مثل : non convertible

cording to Properties of Synthetic Polymers we
n devide area of application into (

Plastic Are Poly molaric solid materials That are glassy and relatively stiFF at r.Temp

Classification of polymers:

There are anumber of methods of classifying polymers. One is to adopt the approach of using thier response to thermal treatment and to divide them into thermoplastics and thermo setes. Thermoplastics are polymers which melt when heated and resolidify when cooled, while thermosets are those which do not melt when heated but, at sufficiently high temp. decompose irreversibly. This system has the benefit that there is a useful chemical distinction between the two groups Thermoplastics comprise essentially linear or lightly branched polymer molecules, while thermosets are substentially crosslinked materials consisting of an extensive 3-D network of covalent chemical bonding.

Another classification system, first suggest by Carothers in 1929, is based on the nature of the chemical reactions employed in the polymerisation. Here the two major groups are the condensation and the addition Polimers.

Free Radical Polymerisation

Polymerization Reactions

البلمرة تحتاج دائماً Catalyst أو بادئ Initiator

Requires catalyst or Initiator

Initiator : تكون Free radical Polymn

Catalyst : = Anionic Polymn
Cation =
Coordination =
ring opening =

Free radical Initiators are

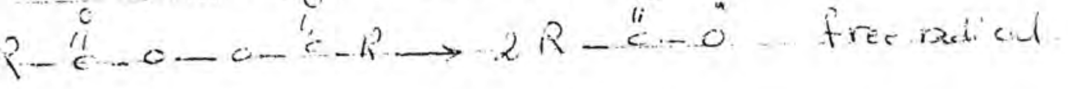
* Peroxides R-O-O-R ضعيفة

الآصرة O—O الطاقة تكسر الى 2RO˙ [illegible]

تكسر الآصرة O—O free radical [illegible]

وعندها تتكون free radical

* بيروكسيد di acyle Peroxidi [illegible]

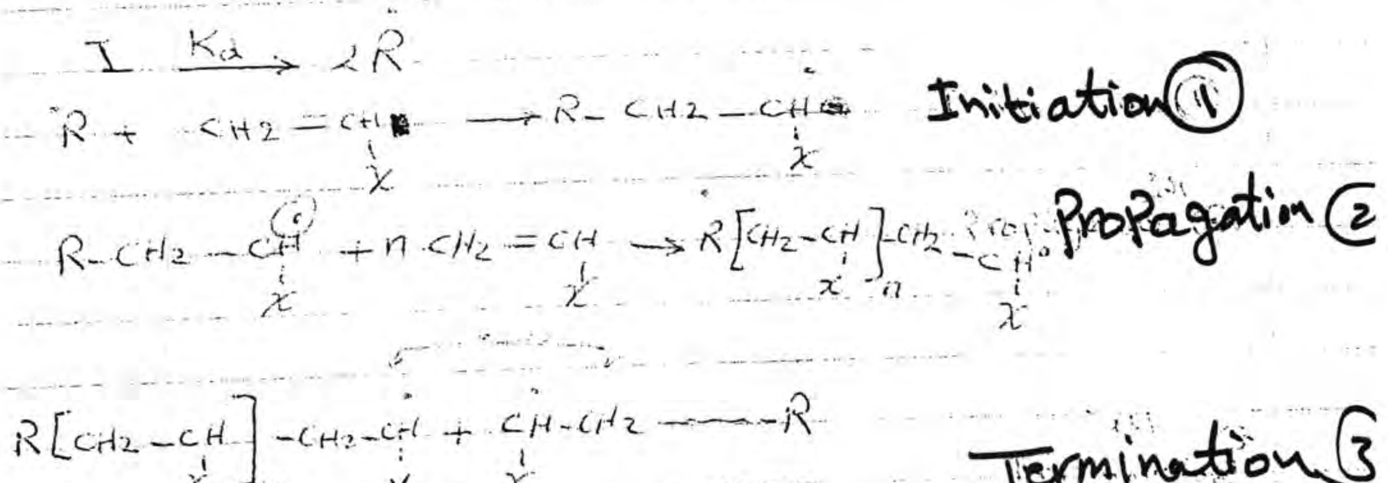


$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-\dot{O}$$ free radical

* per sulfate [illegible]

[illegible] free radical

Mechanism of free radical Polymn



$$I \xrightarrow{K_d} 2\dot{R}$$

$$\dot{R} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$ Initiation ①

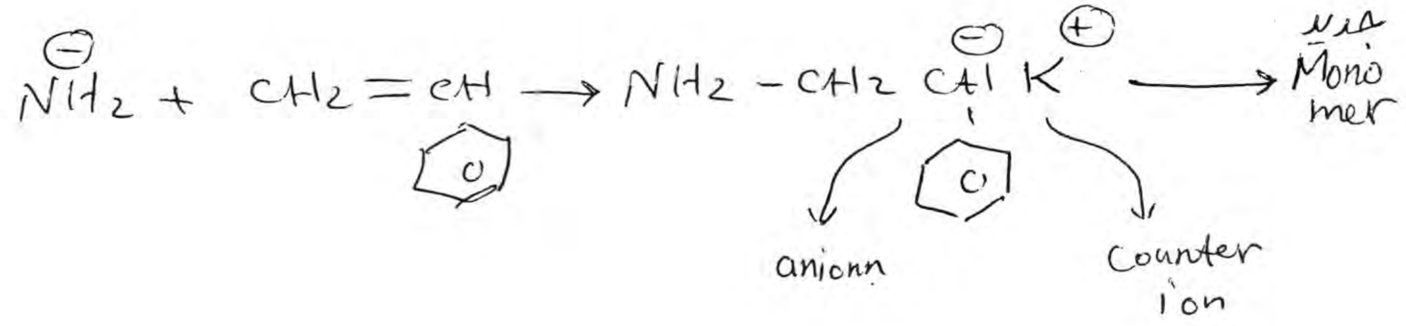
$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + n\,CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$ Propagation ②

$$R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \underset{X}{\underset{|}{\dot{C}H}}-CH_2 \sim\sim R$$ Termination ③

Ionic Polymerization

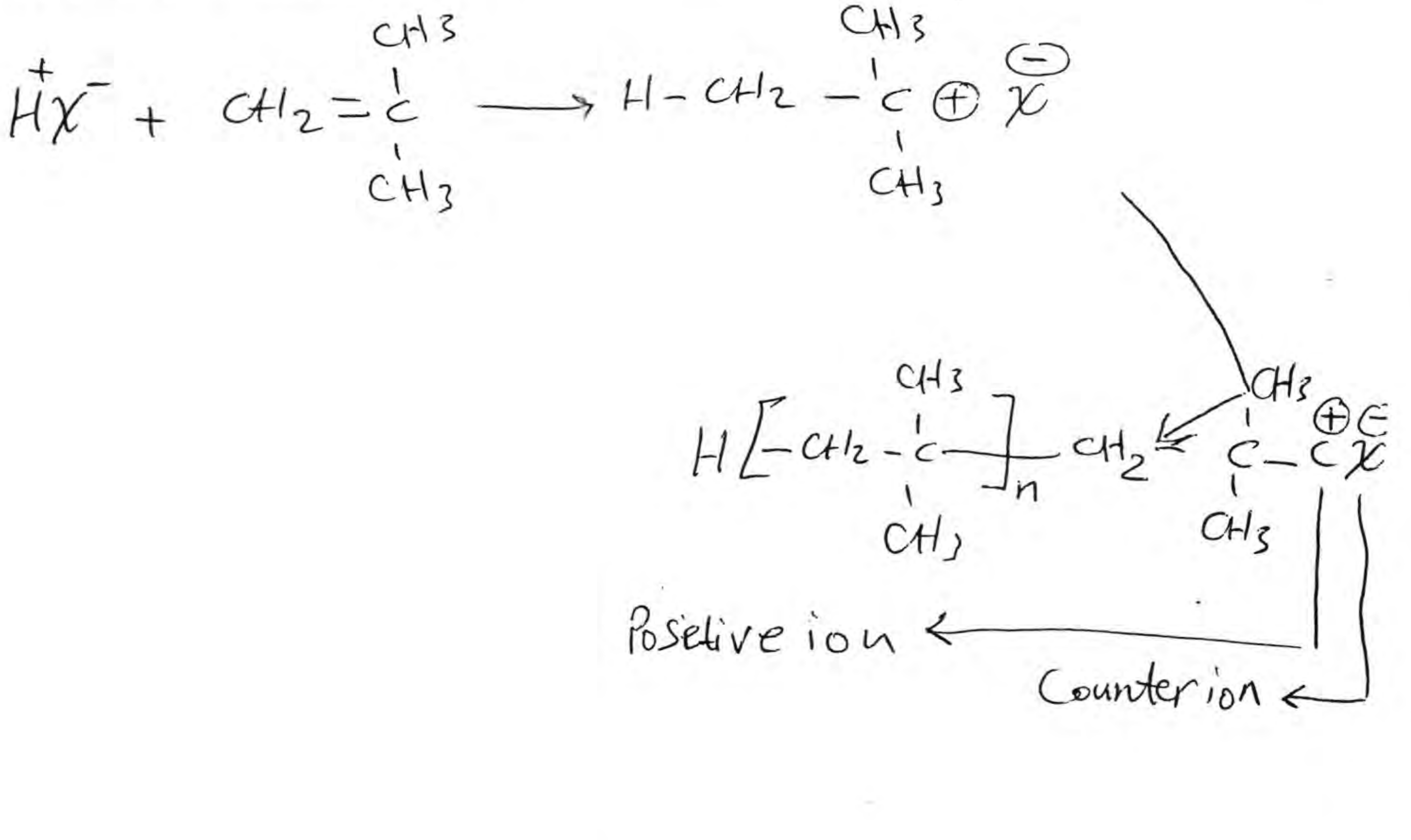
Anoinic Polymerization:-

Na or $KNH_2 \rightarrow K^+ + \bar{N}H_2$



Cationic Polymerization

Protonic acid : $\overset{+}{H}\overset{-}{X}$, $\overset{+}{H}\overset{-}{Cl}$, $\overset{+}{H}\,\overset{-}{HSO_4}$, $\overset{+}{H}\,\overset{-}{H_2SO_4}$



$$\overset{+}{H}\overset{-}{X} + CH_2=\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H-CH_2-\underset{CH_3}{\overset{CH_3}{C}}\oplus\overset{\ominus}{X}$$

$$H\left[-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\right]_n CH_2 \leftarrow \underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}\overset{\ominus}{X}$$