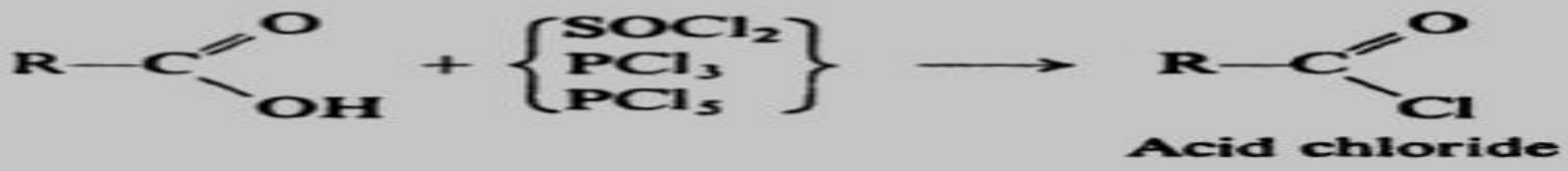
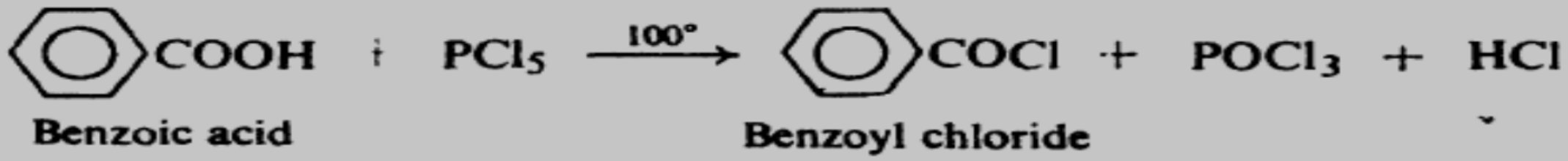
2. Conversion into functional derivatives

(Carboxylic acid derivatives)

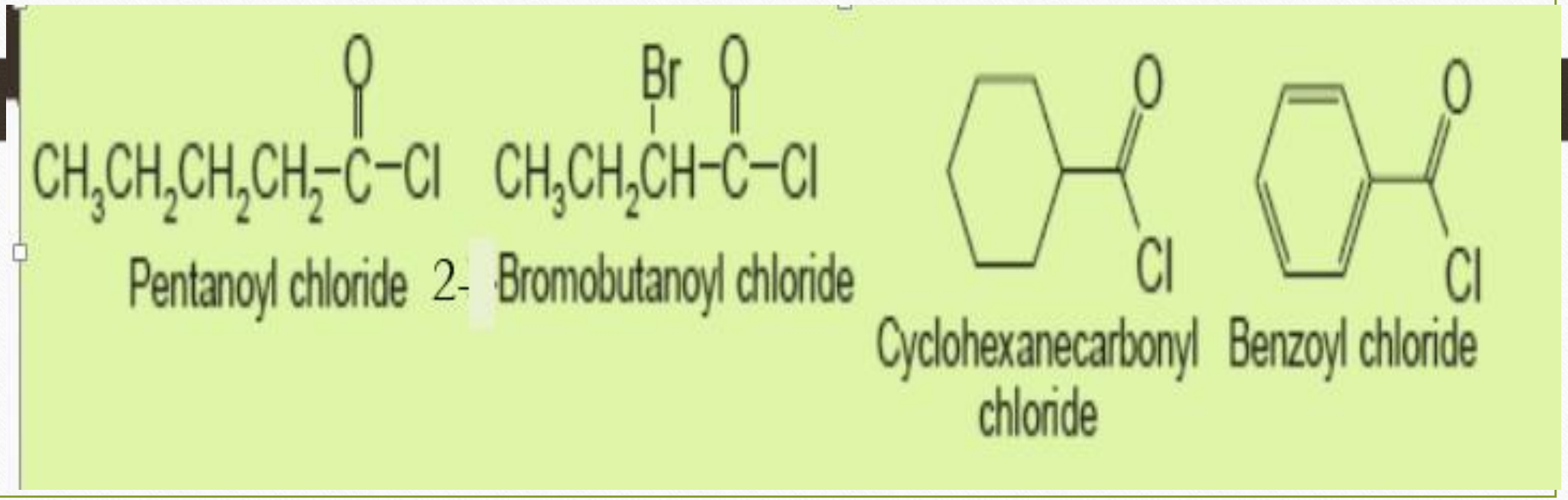
(a) Conversion into acid chlorides.



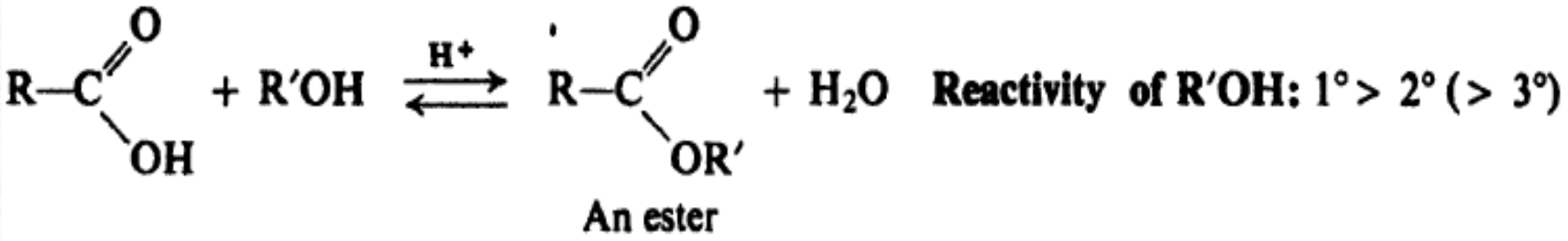


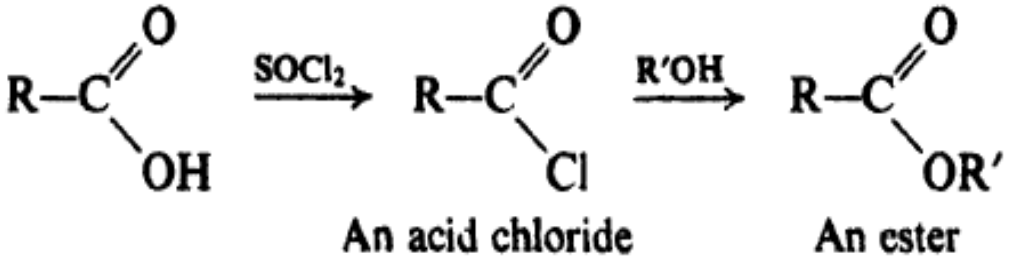
Nomenclature of acid chlorides

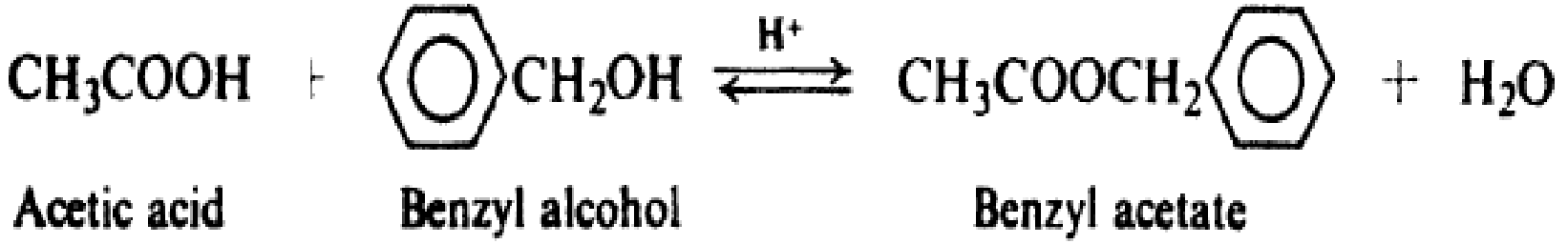
Acid chlorides are named by replacing the -ic acid ending with -yl choride or replacing the carboxylic acid ending with -carbonyl chloride.



b- Conversion into esters.







Nomenclature of esters

- **The mechanism of esterification is necessarily the exact reverse of the mechanism of hydrolysis of esters.**

Reactivity in esterification

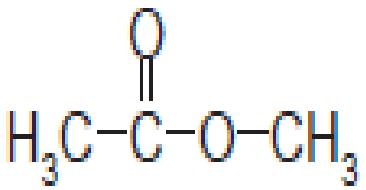
(CH3OH > 1 > 2> 3)

HCOOH > CH_3COOH > RCH_2COOH > $R_2CHCOOH$ > R_3CCOOH

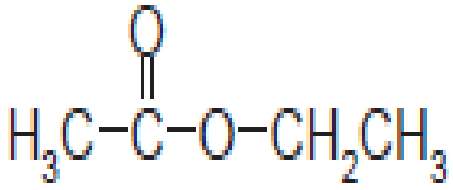
Nomenclature of esters

The first word of the name comes from the alkyl group of the alcohol, and the second part comes from the carboxylate group of the carboxylic acid used.

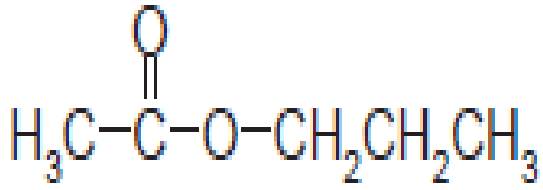
Nomenclature of esters



Methyl acetate
Methylethanoate

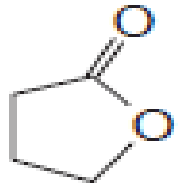


Ethyl acetate
Ethylethanoate



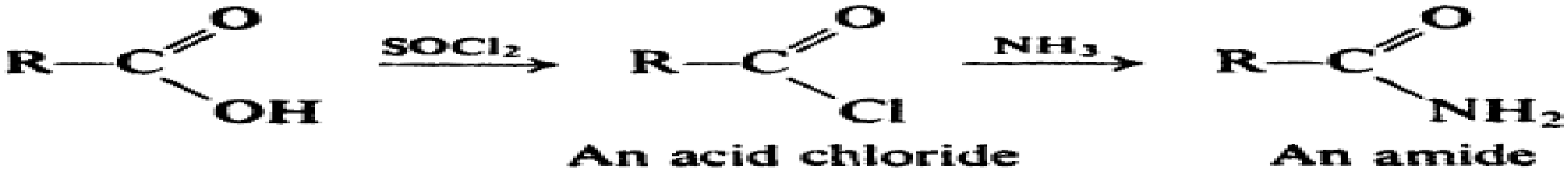
Propyl acetate
Propylethanoate

A cyclic ester is called a lactone, and the IUPAC names of lactones are derived by adding the term lactone at the end of the name of the parent carboxylic acid.



4-Hydroxybutanoic acid lactone

- (c) Conversion into amides.



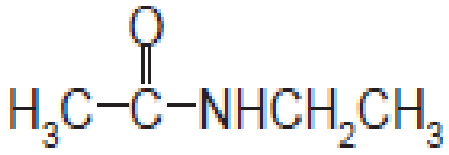
$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow{NH_3} C_6H_5CH_2CONH_2$

Phenylacetic acid — Phenylacetyl chloride — Phenylacetamide

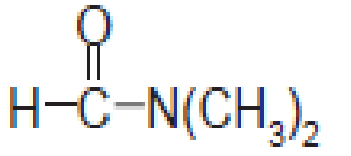
Nomenclature of amides

Amides are named by replacing the -oic acid or -ic acid suffix of the parent carboxylic acids with the suffix -amide, or by replacing the -carboxylic acid ending with -carboxamide.

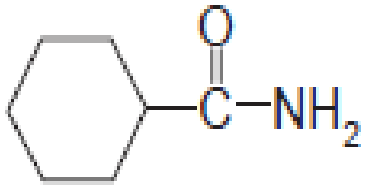
Alkyl groups on nitrogen atoms are named as substituents, and are prefaced by N-or N,N-, followed by the name(s) of the alkyl group(s).



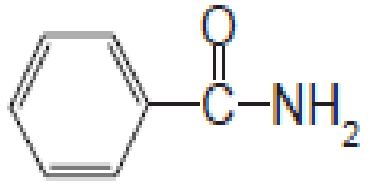
N-Ethylethanamide



N,*N*-Dimethylformamide
DMF



Cyclohexanecarboxamide



Benzamide

Preparation of acid anhydrides

Only one monocarboxylic acid anhydride is encountered very often: **acetic anhydride**

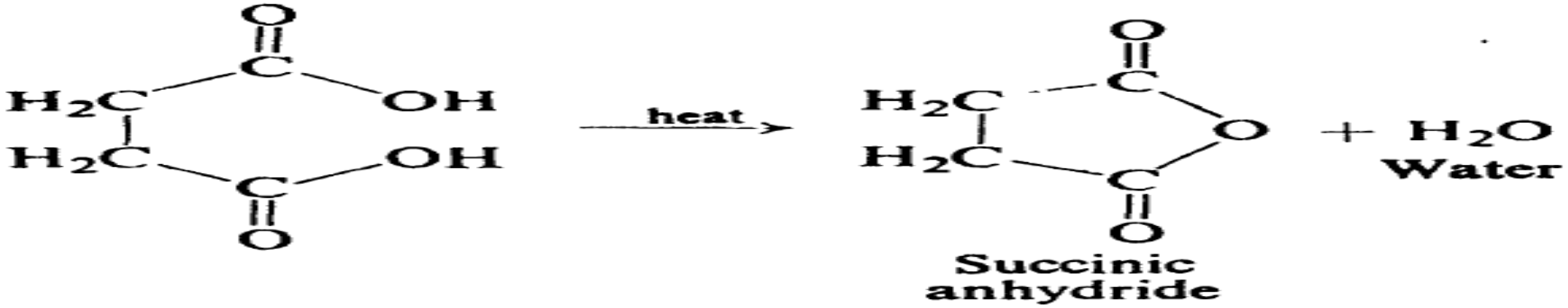
$$CH_3COOH \xrightarrow[700^\circ]{AlPO_4} H_2O + \underset{\text{Ketene}}{CH_2{=}C{=}O} \xrightarrow{CH_3COOH} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

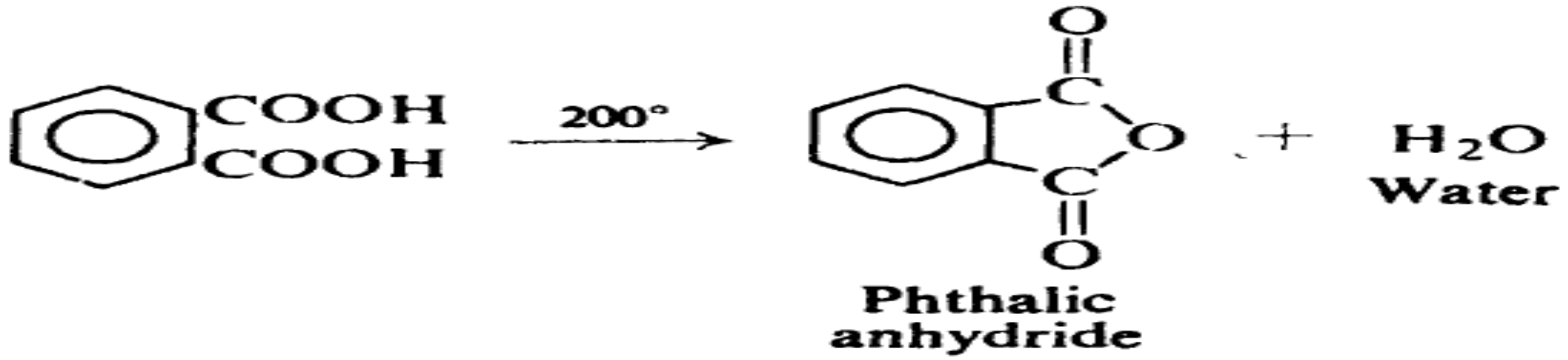
Ketene is made in the laboratory by pyrolysis of acetone, and ordinarily used as soon as it made

$$CH_3COCH_3 \xrightarrow{700\text{–}750^\circ} CH_4 + \underset{\text{Ketene}}{CH_2{=}C{=}O}$$

Preparation of acid anhydrides

- Dicarboxylic acids yield anhydrides on simple heating: in those cases where a five- or six-membered ring

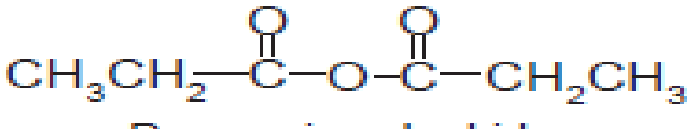




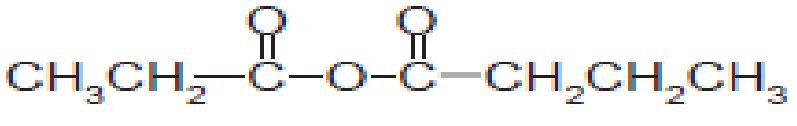
Nomenclature of acid anhydrides

Replacing the -acid suffix of the parent carboxylic acids with the word anhydride.

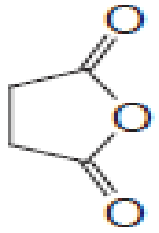
Mixed anhydrides that consist of two different acid-derived parts are named using the names of the two individual acids with an alphabetical



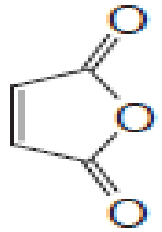
Propanoic anhydride



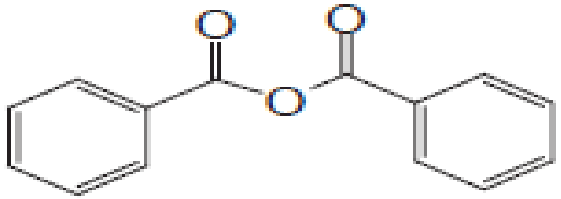
Butanoic propanoic anhydride



Butanedioicanhydride
Succinic anhydride



2-Butenedioic anhydride
Maleic anhydride

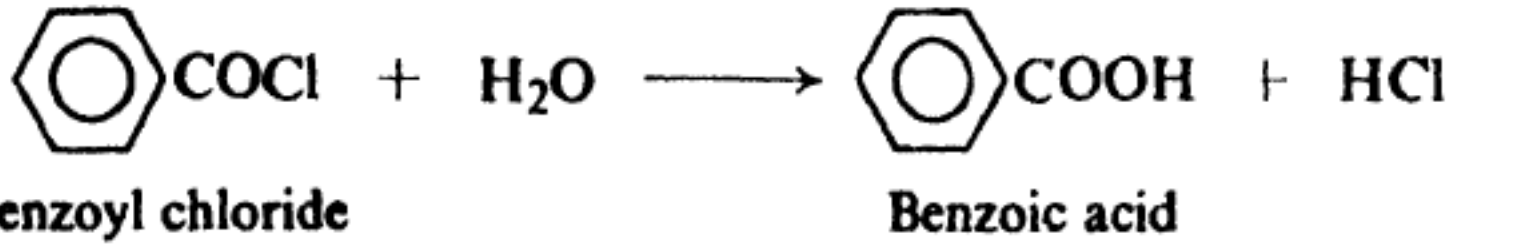


Benzoic anhydride

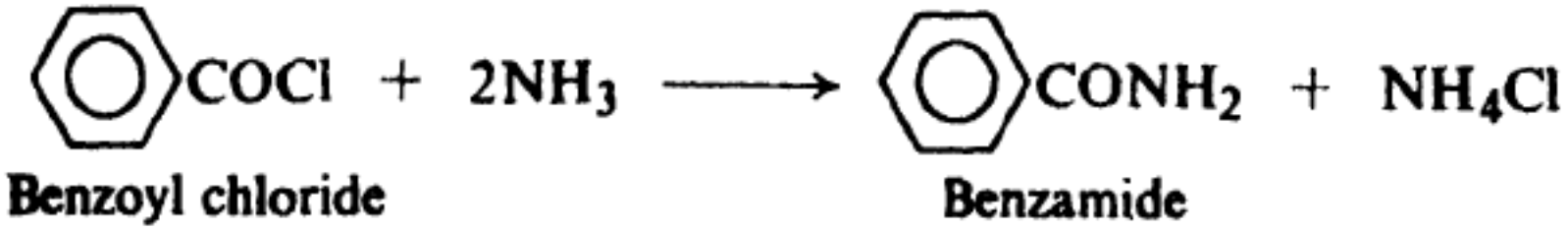
1-Reaction of acid chloride

1-Conversion into acid and acid derivative.

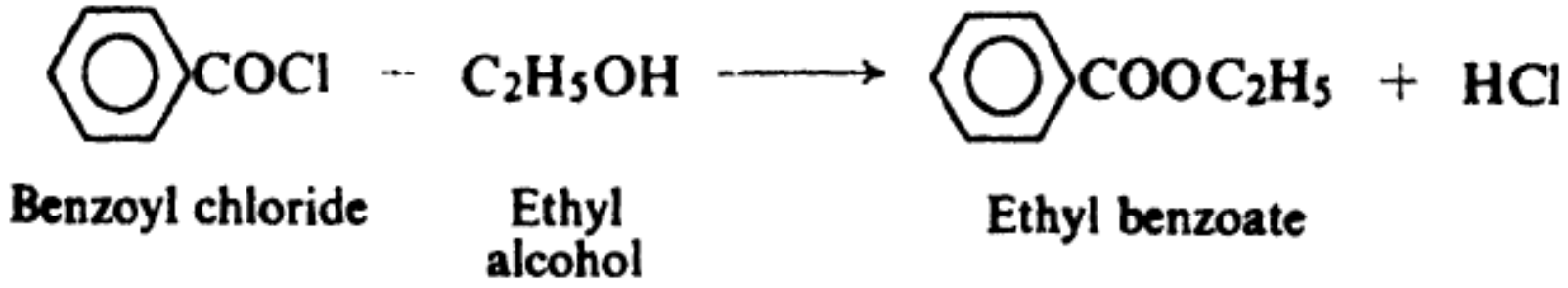
(a) Conversion into acids. Hydrolysis



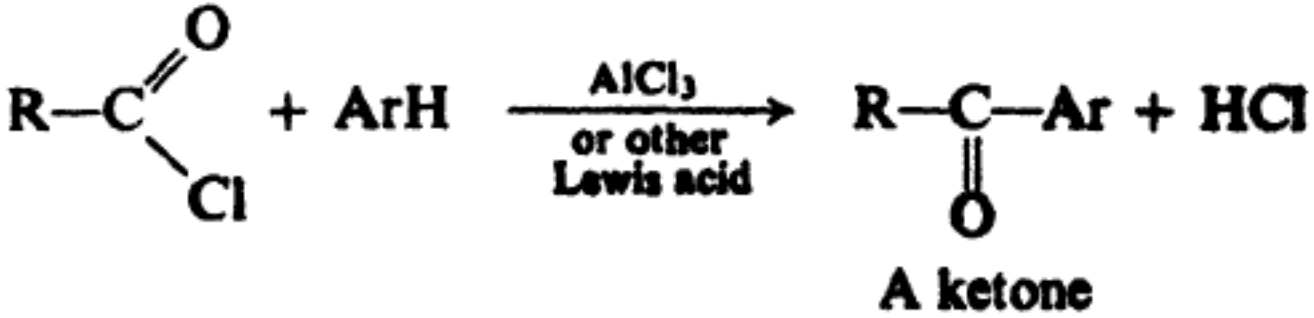
(b) Conversion into amides. Ammonolysis



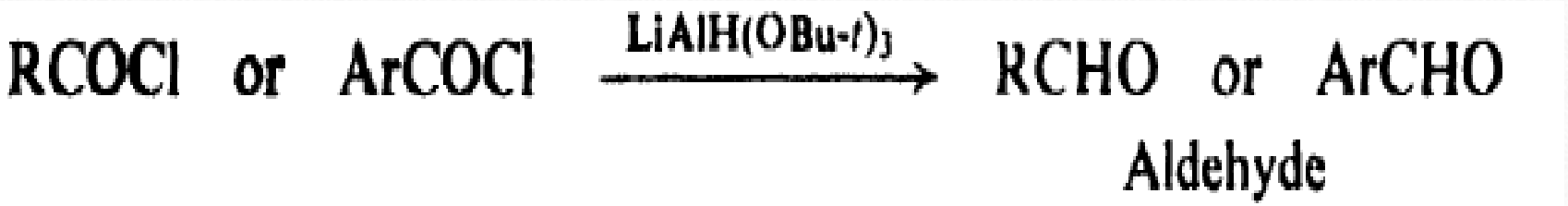
(c) Conversion into esters. Alcoholysis



2. Formation of ketones. Friedel-Crafts acylation.

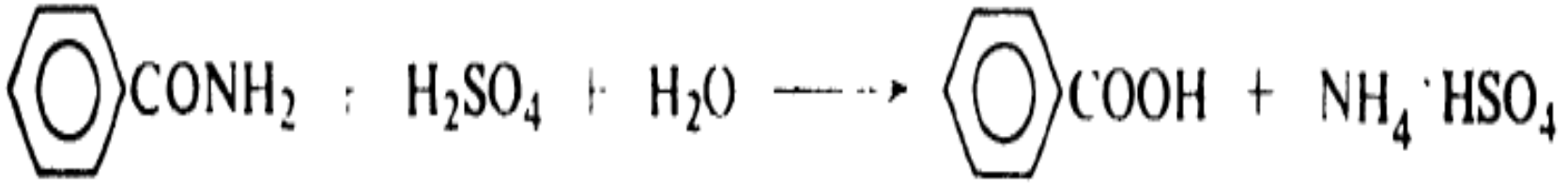


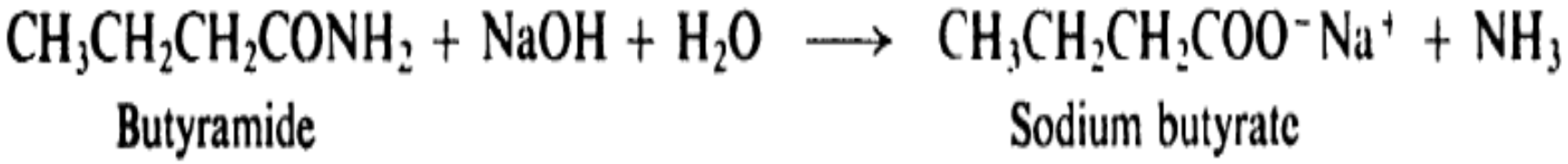
3-Formation of aldehydes by reduction.



2-Reaction of amide

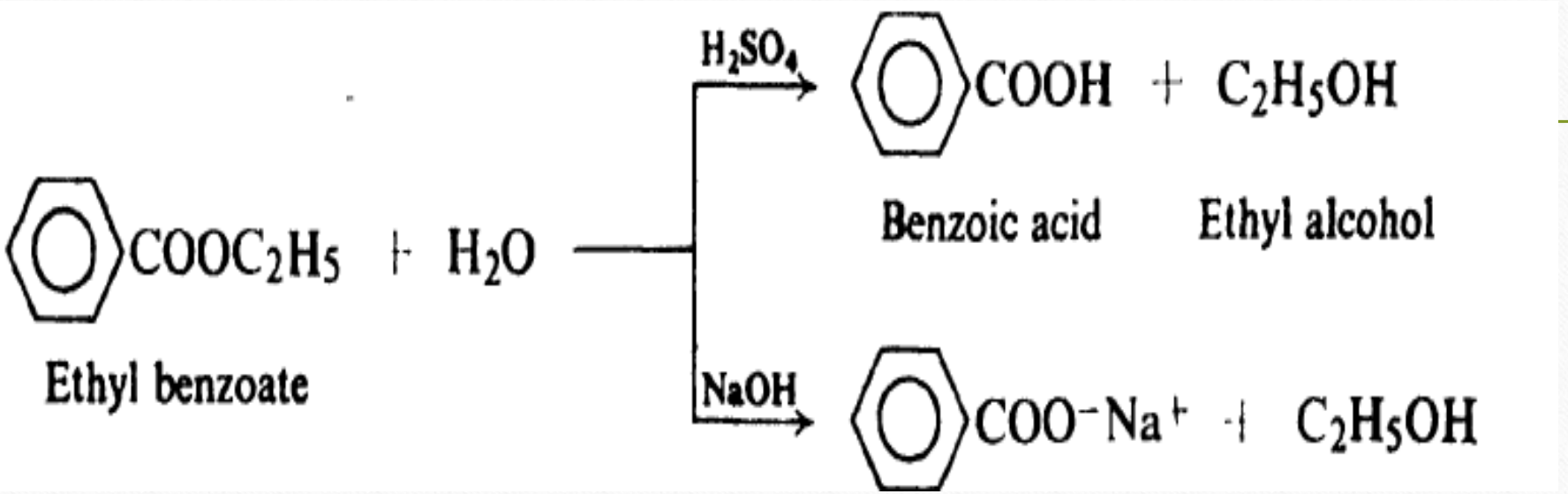
1. Hydrolysis





2-Reacation of ester

(a) Conversion into acids. Hydrolysis

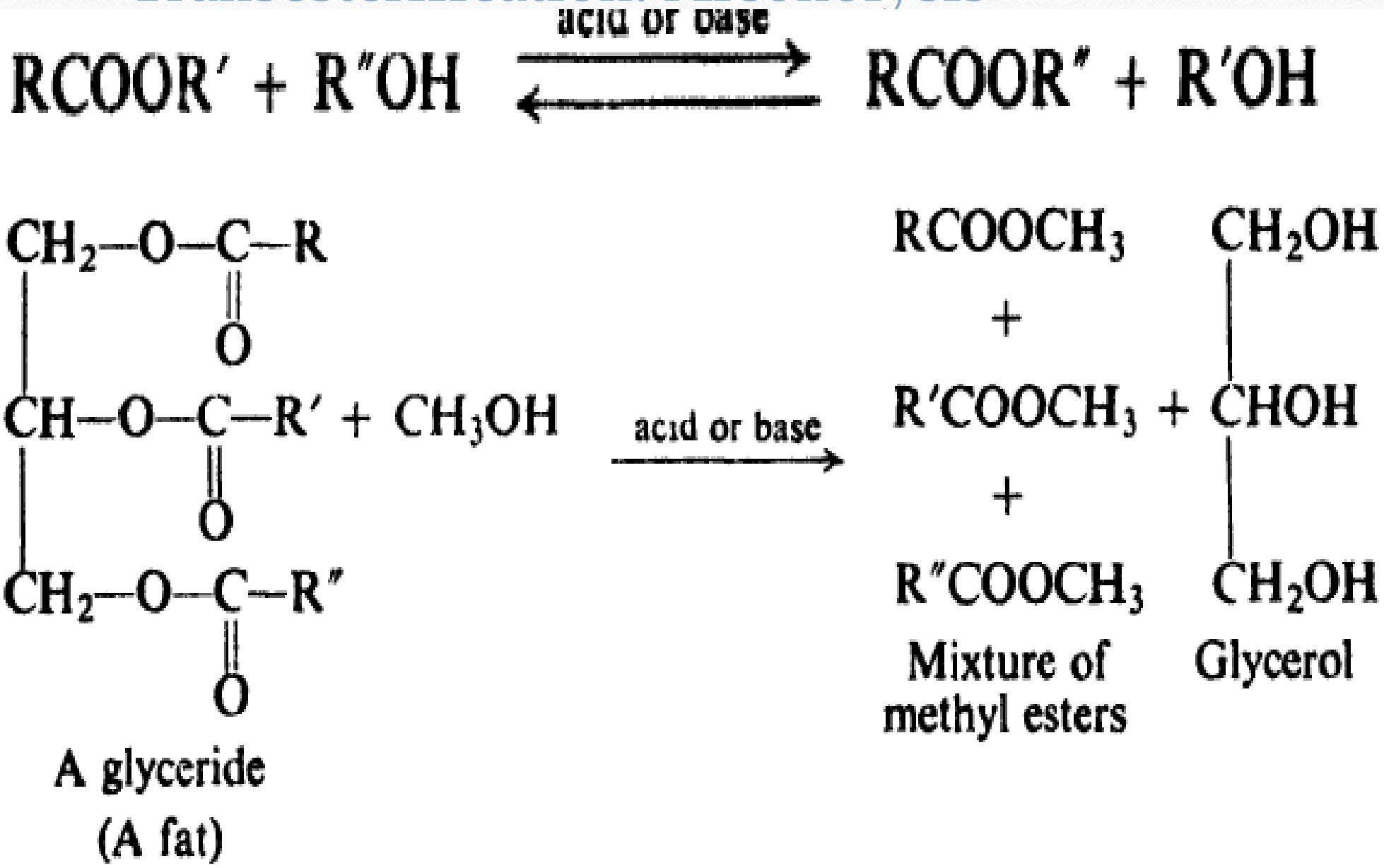


(b) Conversion into amides. Ammonolysis

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

Ethyl acetate — Acetamide — Ethyl alcohol

(c) Conversion into esters: Transesterification. Alcoholysis



3-Reaction of acid anhydrides

1. Conversion into acids and acid derivatives

$$(RCO)_2O + HZ \longrightarrow RCOZ + RCOOH$$

(a) Conversion into acids. Hydrolysis

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

Acetic anhydride — Acetic acid

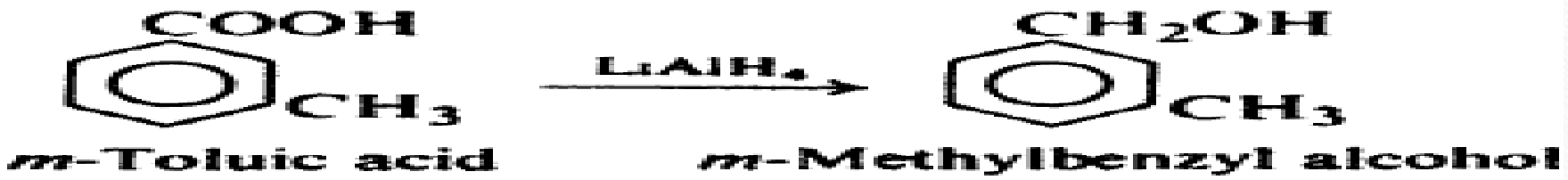
(b) Conversion into amides. Ammonolysis

$$(CH_3CO)_2O + 2NH_3 \longrightarrow CH_3CONH_2 + CH_3COO^-NH_4^+$$

Acetic anhydride — Acetamide — Ammonium acetate

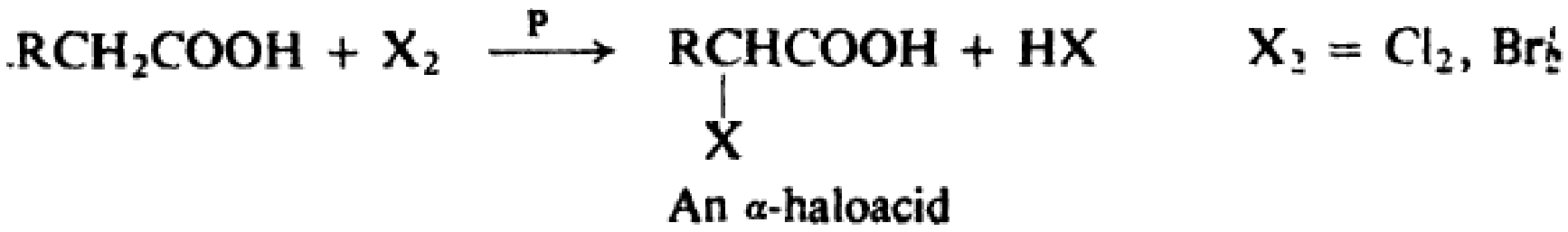
3. Reduction

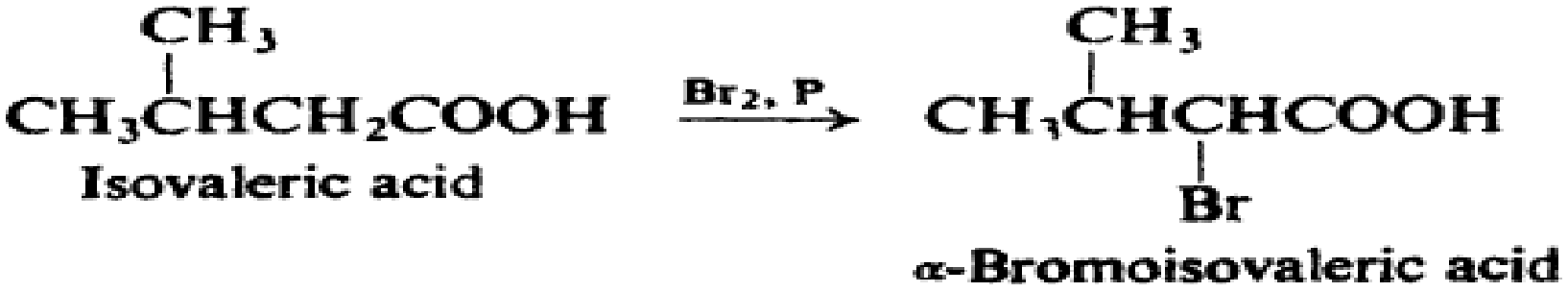
One of the few reducing agents capable of reducing an acid directly to an alcohol is lithium aluminum hydride, $LiAlH_4$



4. Substitution in alkyl or aryl group

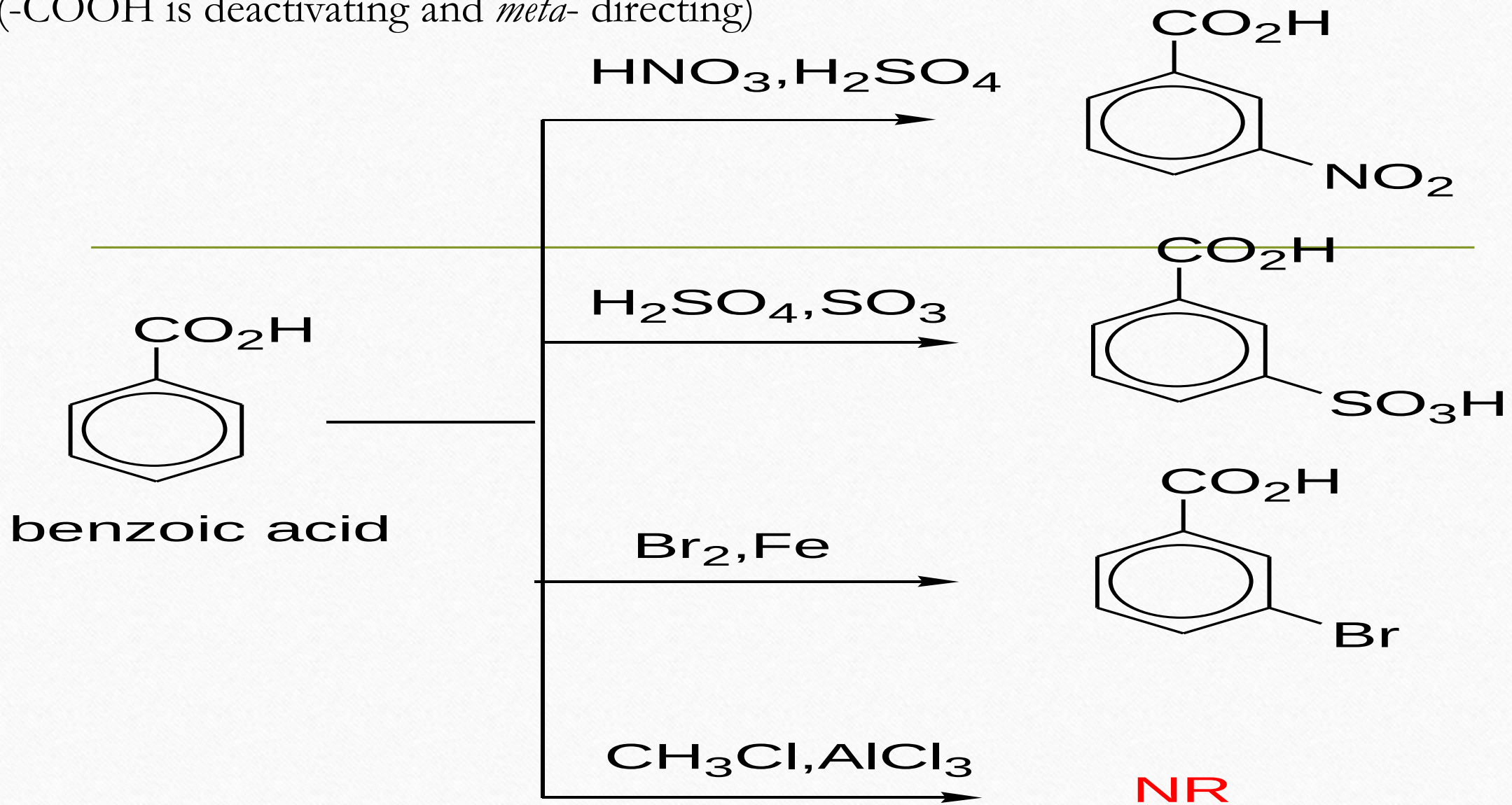
a- Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction





b-Ring substitution in aromatic acids (Electrophilic aromatic substitution)

(-COOH is deactivating and *meta*- directing)



Dicarboxylic acids

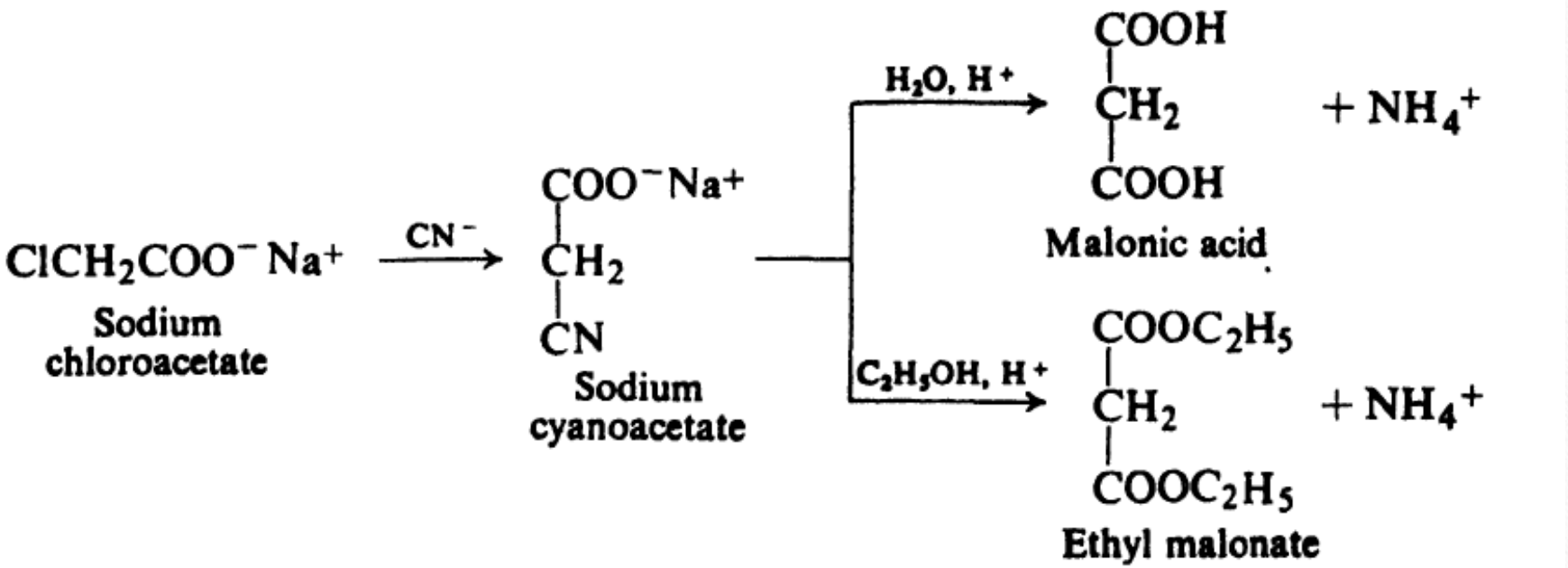
If the substituent is a second carboxyl group, we have a dicarboxylic acid. For example:

$HOOCCH_2COOH$	$HOOC(CH_2)_2COOH$,	$HOOC(CH_2)_4COOH$
Malonic acid	**Succinic acid**	**Adipic acid**
Propanedioic acid	**Butanedioic acid**	**Hexanedioic acid**

- **Table 2 Dicarboxylic acid**

Name	Formula
Oxalic	HOOC—COOH
Malonic	$HOOCCH_2COOH$
Succinic	$HOOC(CH_2)_2COOH$
Glutaric	$HOOC(CH_2)_3COOH$
Adipic	$HOOC(CH_2)_4COOH$
Maleic	*cis*-HOOCCH=CHCOOH
Fumaric	*trans*-HOOCCH=CHCOOH

Preparation of Dicarboxylic acid



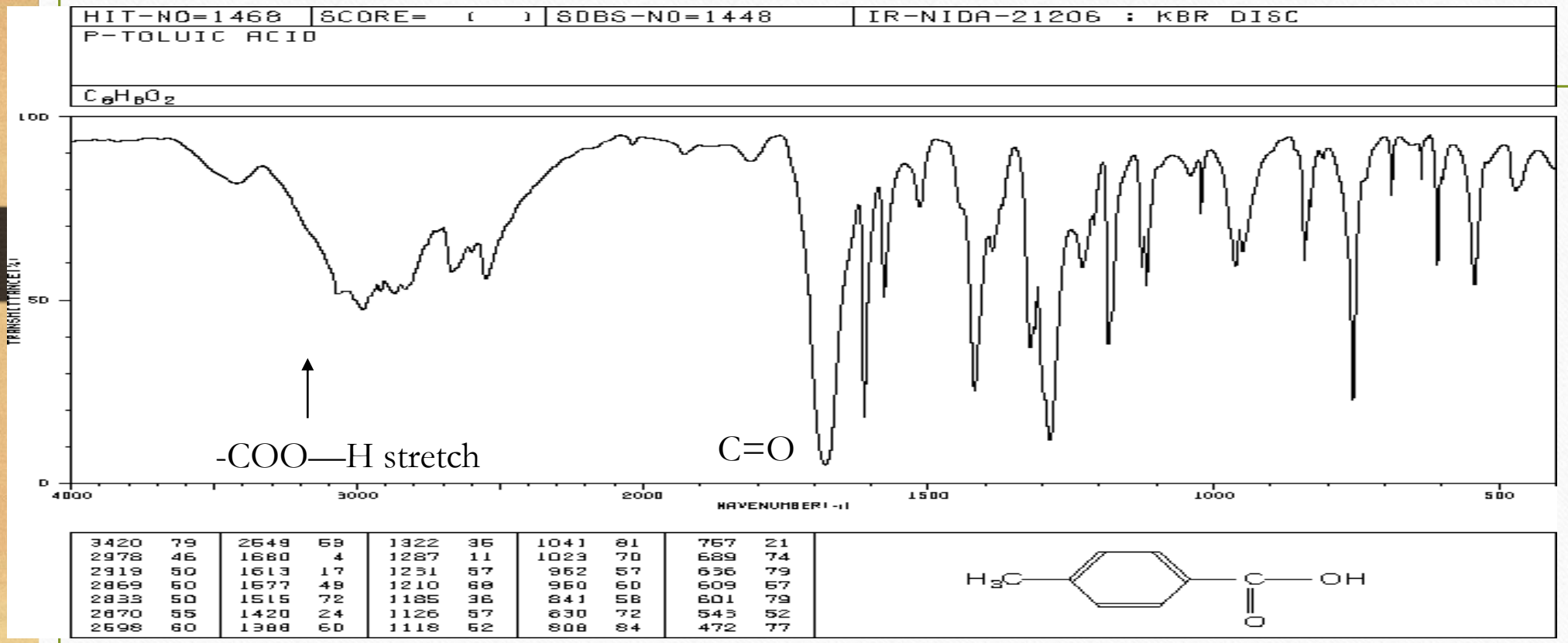
Spectroscopy

- IR: -COOH O—H stretch 2500 – 3000 cm^{-1} (b)

  C=O stretch 1680 – 1725 (s)

- nmr: -COOH 10.5 – 12 ppm

IR SPECTRUM of p-toluic acid



3420	79	2649	59	1322	36	1041	81	757	21
2978	46	1680	4	1287	11	1023	70	689	74
2919	50	1613	17	1231	57	962	57	636	79
2869	50	1577	49	1210	68	950	60	609	67
2833	50	1515	72	1185	36	841	58	601	79
2870	55	1420	24	1126	57	830	72	543	52
2698	60	1388	60	1118	62	808	84	472	77

NMR Spectrum of p-toluic acid