Chapter 17 – Carboxylic Acids and Their Derivatives
Chem 306
Roper

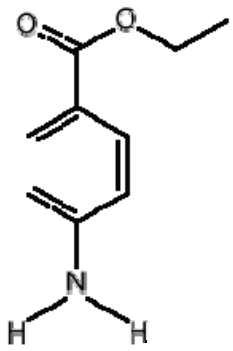
I. Overview

A. Carboxylic acid functional groups contain the carboxyl structural feature.

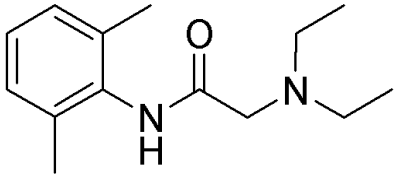
1. Features of the carboxyl group

2. The reactivity of the carboxyl group

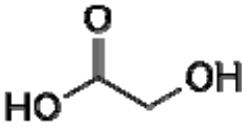
B. Carboxylic acids and their derivatives are very prevalent in pharmaceuticals, consumer products, and the natural world.



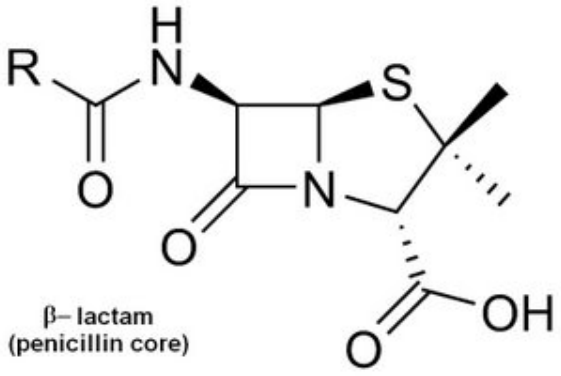
benzocaine



lidocaine



glycolic acid



II. Carboxylic Acids (RCOOH)

A. Nomenclature

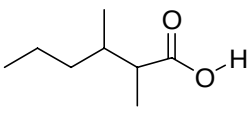
1. For IUPAC naming, the longest carbon chain should contain the COOH group. The names end in “oic acid.

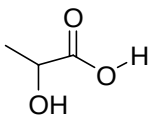
2. Common names – know formic, acetic, propionic, butyric, oxalic, citric, lactic, salicylic, and benzoic acids and the fatty acids discussed in class.

3. The table below lists some aliphatic carboxylic acids and their common names.

Structure	IUPAC Name	Common Name	Derivation
$HCOOH$	methanoic acid	formic acid	Latin: *formica,* ant
CH_3COOH	ethanoic acid	acetic acid	Latin: *acetum,* vinegar
CH_3CH_2COOH	propanoic acid	propionic acid	Greek: *propion,* first fat
$CH_3(CH_2)_2COOH$	butanoic acid	butyric acid	Latin: *butyrum,* butter
$CH_3(CH_2)_3COOH$	pentanoic acid	valeric acid	Latin: *valere,* to be strong
$CH_3(CH_2)_4COOH$	hexanoic acid	caproic acid	Latin: *caper,* goat
$CH_3(CH_2)_6COOH$	octanoic acid	caprylic acid	Latin: *caper,* goat
$CH_3(CH_2)_8COOH$	decanoic acid	capric acid	Latin: *caper,* goat
$CH_3(CH_2)_{10}COOH$	dodecanoic acid	lauric acid	Latin: *laurus,* laurel
$CH_3(CH_2)_{12}COOH$	tetradecanoic acid	myristic acid	Greek: *myristikos,* fragrant
$CH_3(CH_2)_{14}COOH$	hexadecanoic acid	palmitic acid	Latin: *palma,* palm tree
$CH_3(CH_2)_{16}COOH$	octadecanoic acid	stearic acid	Greek: *stear,* solid fat
$CH_3(CH_2)_{18}COOH$	eicosanoic acid	arachidic acid	Greek: *arachis,* peanut

Name these acids





4. Some acids are di and tri-protic

Oxalic acid (ethanedioc acid)

Succinic Acid (butanedioc acid)

Citric Acid (2 – hydroxy – 1,2,3 – propanetricarboxylic acid)

5. Many drugs and food additives are salts of the acids above. Name the anion (conjugate base) component of each of the acids above.

B. Physical Properties

Rank the following in order of increasing solubility in water.

acetic acid 1 – propanol propanal propane

Oxalic acid, a two carbon acid, has a boiling temperature range of 149 – 160 °C. Why is boiling temperature so much higher than for acetic acid (118 °C)?

C. Acidic Behavior of RCOOH

1. Review – K_a (acid dissociation constant)

2. Table of K_a and pk_a values for some weak acids. (pKa = - log[ka])

Formula	Name	K_a	pK_a
H_3PO_4	Phosphoric acid	7.5×10^{-3}	2.12
HCOOH	Formic acid	1.8×10^{-4}	3.75
$CH_3CH(OH)COOH$	Lactic acid	1.4×10^{-4}	3.86
CH_3COOH	Acetic acid	1.8×10^{-5}	4.75
H_2CO_3	Carbonic acid	4.3×10^{-7}	6.37
$H_2PO_4^-$	Dihydrogen phosphate ion	6.2×10^{-8}	7.21
H_3BO_3	Boric acid	7.3×10^{-10}	9.14
NH_4^+	Ammonium ion	5.6×10^{-10}	9.25
HCN	Hydrocyanic acid	4.9×10^{-10}	9.31
C_6H_5OH	Phenol	1.3×10^{-10}	9.89
HCO_3^-	Bicarbonate ion	5.6×10^{-11}	10.25
HPO_4^{2-}	Hydrogen phosphate ion	2.2×10^{-13}	12.66

A stronger acid has a _____Ka but a _____pKa.

T or F Product formation is favored in the aqueous equilibria of the acids listed above.

3. RCOOH's dissociate in water and produce low concentrations of H3O+ and a resonance stabilized carboxylate anion.

4. The substituents of a RCOOH can increase or decrease acidity.

A. Explain the trend below.

Formula:	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH
Name:	Acetic acid	Chloroacetic acid	Dichloroacetic acid	Trichloroacetic acid
pK_a:	4.76	2.86	1.48	0.70

Compare lactic acid ($K_a = 8.3 \times 10^{-4}$) and propanoic acid ($K_a = 1.26 \times 10^{-5}$)

Compare acetic acid ($K_a = 1.8 \times 10^{-5}$) and glycolic acid ($K_a = 1.5 \times 10^{-4}$).

III. Reactions of RCOOH

A. Reactions with bases (formation of carboxylate salts)

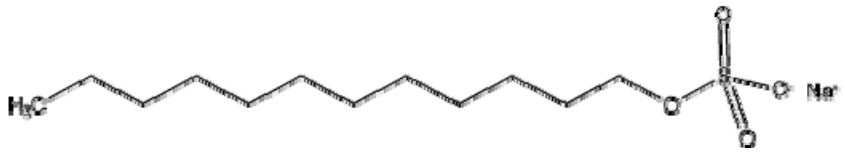
Draw the structures for the following carboxylate salts:

sodium lactate

calcium propionate

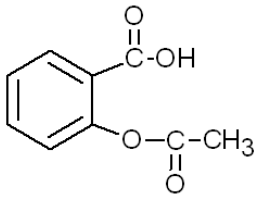
Soap molecules are the sodium salts of fatty acids.

Detergent molecules have a structure very similar to soap.

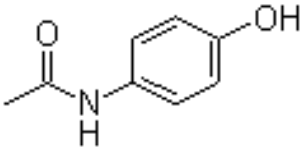


B. Esterification (Ester formation)

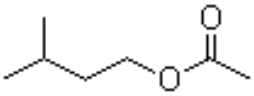
1. Esters – Which of the following contain an ester functional group?



Aspirin



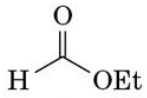
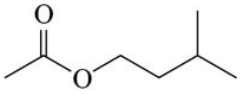
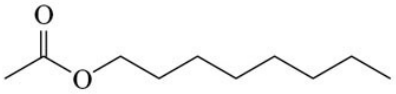
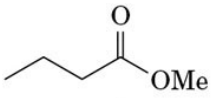
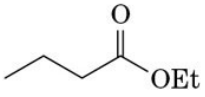
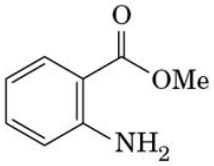
Acetominophen



Isopentylacetate

2. The ester functional group is commonly found in biological molecules (triglycerides, etc.), and polymeric materials (polyester)! Many esters are fragrant and are used as flavoring agents.

Ester Flavoring Agents

Structure	Name	Flavor
	Ethyl formate	Rum
	Isopentyl acetate	Banana
	Octyl acetate	Orange
	Methyl butanoate	Apple
	Ethyl butanoate	Pineapple
	Methyl 2-aminobenzoate (Methyl anthranilate)	Grape

3. Overall Esterification Reaction

What will shift the equilibrium to the right? to the left? (Le Chatlier returns!!)

4. Acid Catalysis

5. Examples of esterification:

a. formic acid + ethanol

b. butanoic acid + methanol

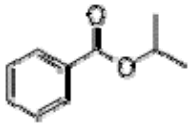
c. salicylic acid + acetic acid

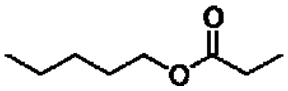
d. What acid and alcohol are used to make the following?

orange flavoring/odor – octyl acetate

wintergreen flavor/odor– methyl benzoate

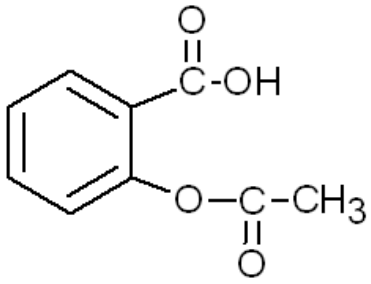
More nomenclature practice!



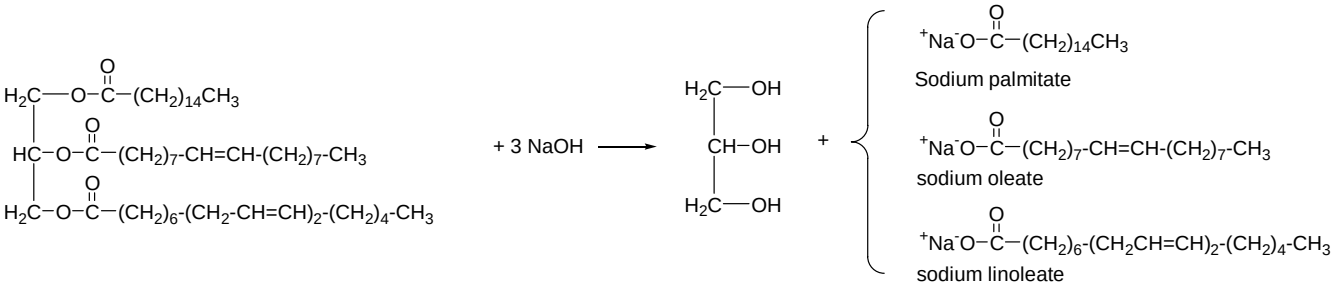


5. Hydrolysis of an ester

What are the hydrolysis products of aspirin (acetylsalicylic acid)?



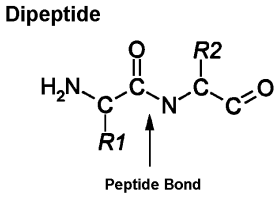
Making soap from fat and lye (NaOH) involves the reaction of an ester with base.

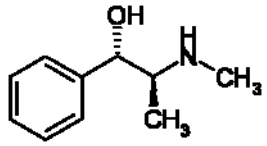


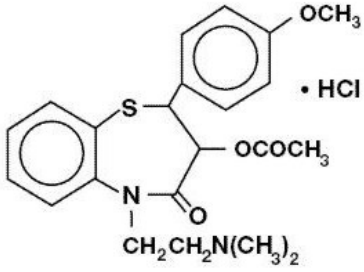
Fat strong base glycerol *soaps*

C. Amide formation

1. Amides – Which of the following contain an amide functional group?







Peptide Bond *Psuedoephedrine* *Cardizem*

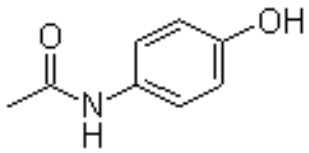
2. Overall Reaction (amide formation)

3. Examples of Amide Formation:

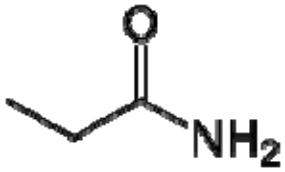
butanoic acid + ammonia

acetic acid + methylamine

What acid is used to make acetaminophen (Tylenol)?



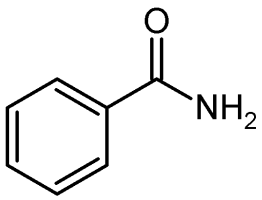
Nomenclature practice

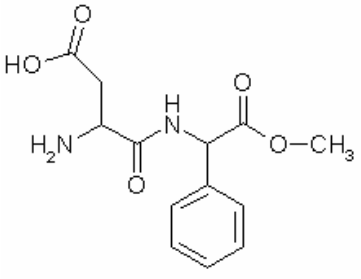


4. Hydrolysis of amides

What are the hydrolysis products of the following?

N – propylacetamide



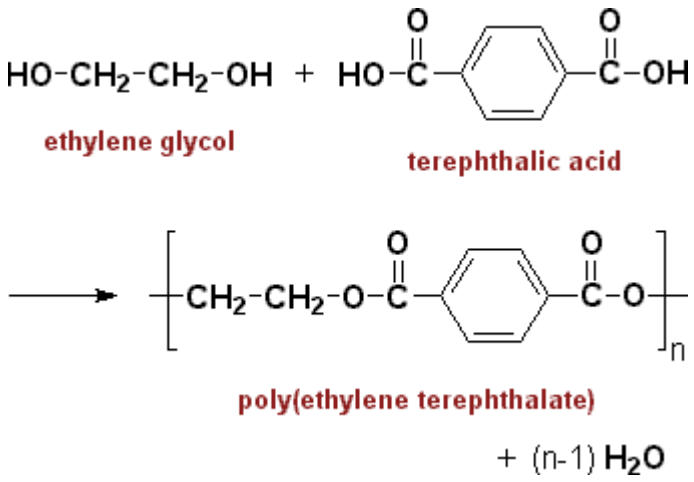


Aspartame

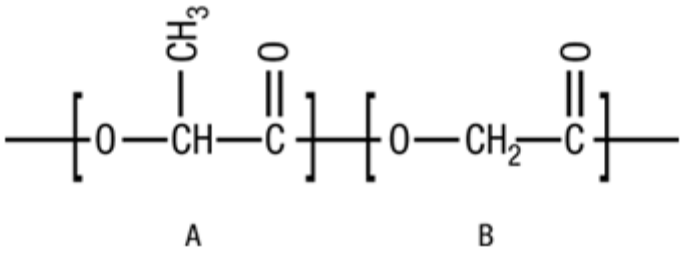
D. Polymer formation – requires difunctional reactants

1. Polyesters

a. PETE – polyethylene terepthalate (a copolymer of ethylene glycol and terephthalic acid)

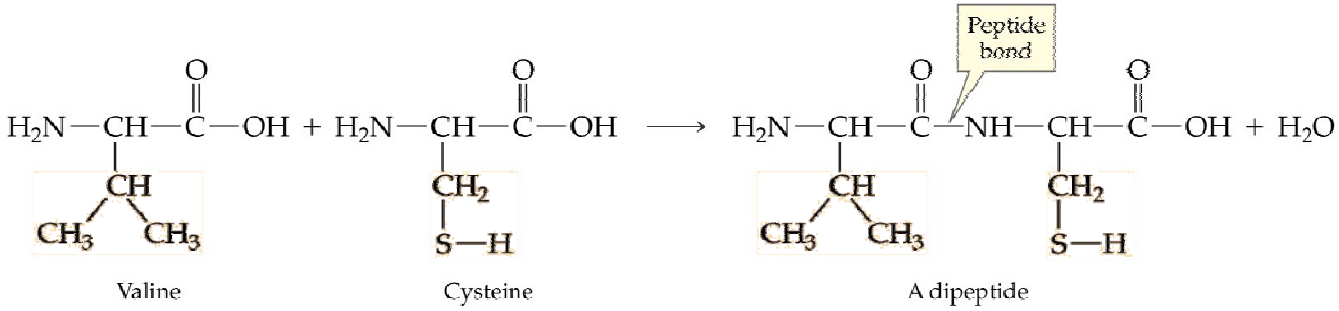


b. Dissolvable stitches are a polyester copolymer of glycolic acid and lactic acid. What makes them dissolvable?



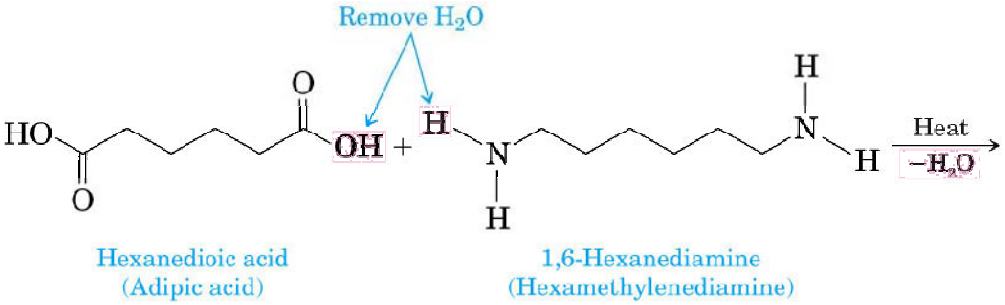
2. Polyamides

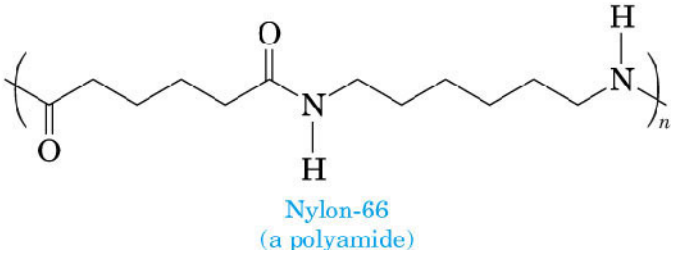
a. Proteins - amino acid monomers are linked by amide bonds



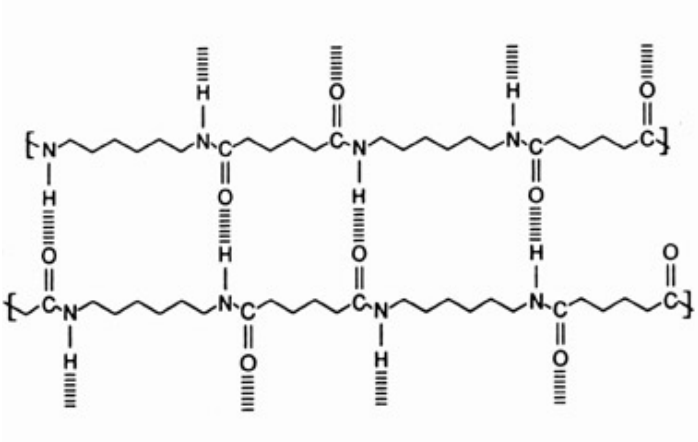
. b. Nylon

Nylon 6,6 – a copolymer of hexamethylene diamine and adipic acid (hexanedioic acid).





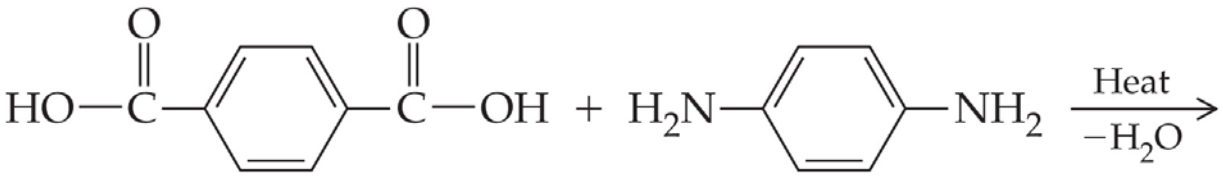
What gives nylon its structural strength?



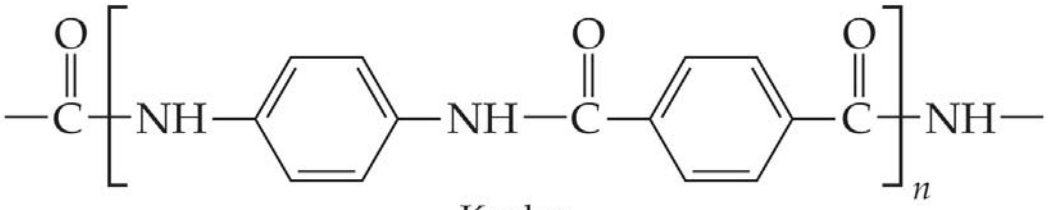
Two videos of the synthesis of nylon

http://www.youtube.com/watch?v=5k_4hMjYoMs
http://www.youtube.com/watch?v=y479OXBzCBQ

b. Kevlar – a copolymer of

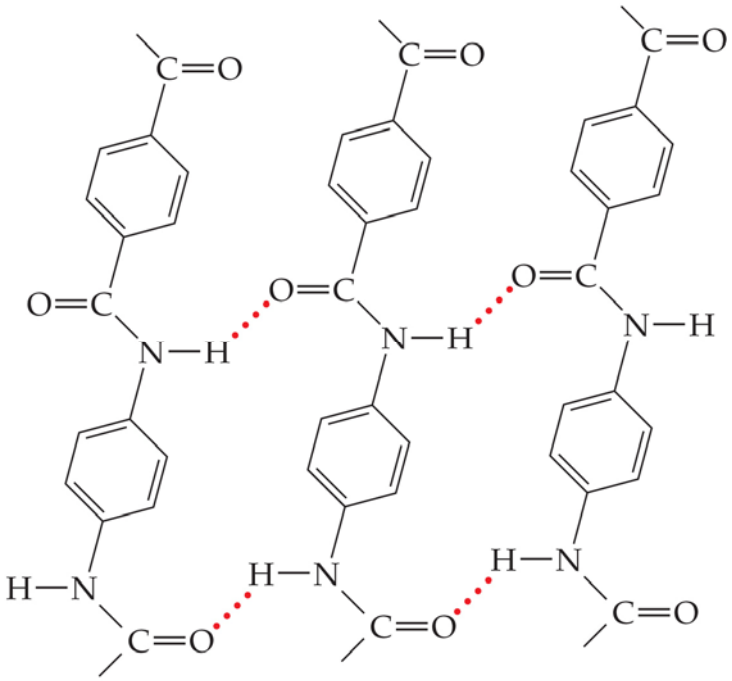


1,4-Benzenedicarboxylic acid 1,4-Diaminobenzene



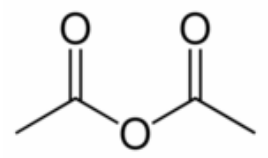
Kevlar

What gives Kevlar its strength?

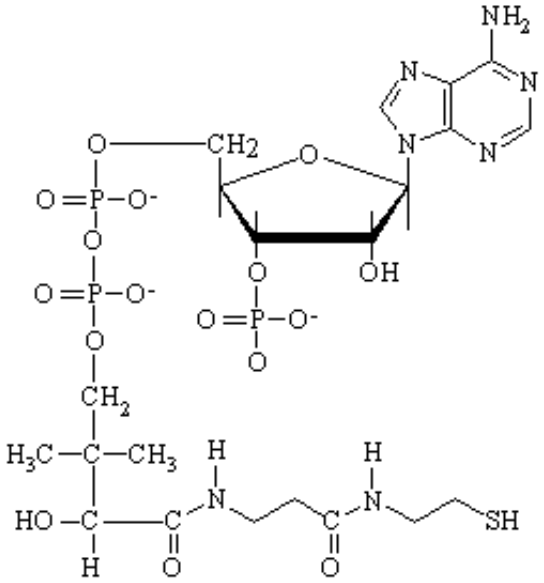


IV. Phosphate Derivatives of RCOOH

A. Phosphoric anhydrides are found in many biological molecules and metabolic intermediates.

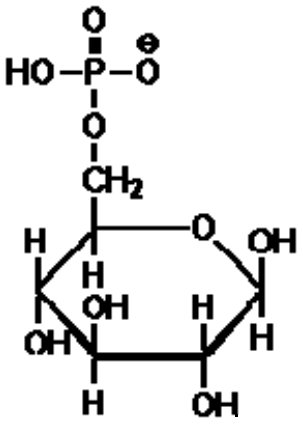


Carbon based anhydride



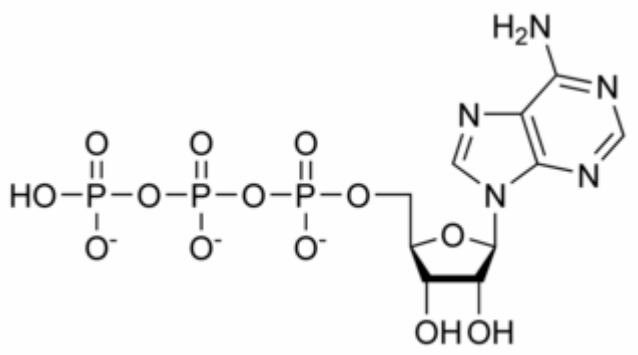
Coenzyme A

B. Phosphoric esters – These are often formed in intermediate compounds in the metabolism of sugars

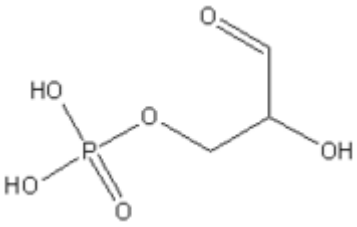


C. Some biologically important organic phosphates

ATP – adenosine triphosphate



Glyceraldehyde – 3 – phosphate



D. In later chapters, we will see that the enzyme-facillitated hydrolysis of a phosphoric anhydride bond in ATP yields energy that is used to fuel other chemical reactions in the body.