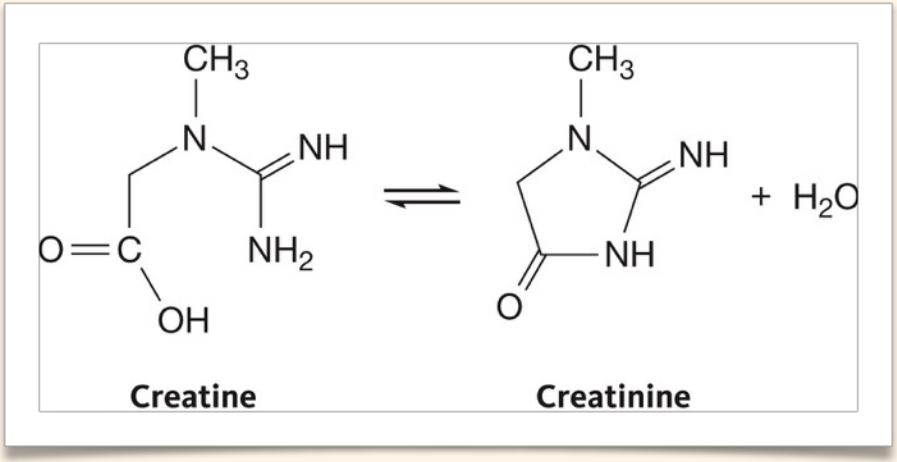
Chem 150, Spring 2015

Unit 8 - Carboxylic Acids and Amines: Organic Acids and Bases

Introduction

- Many biological molecules have functional groups that are acids and bases.



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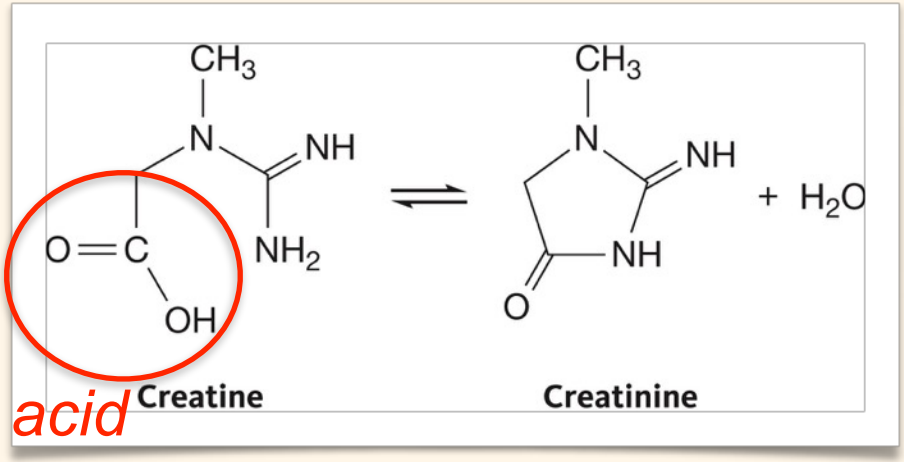

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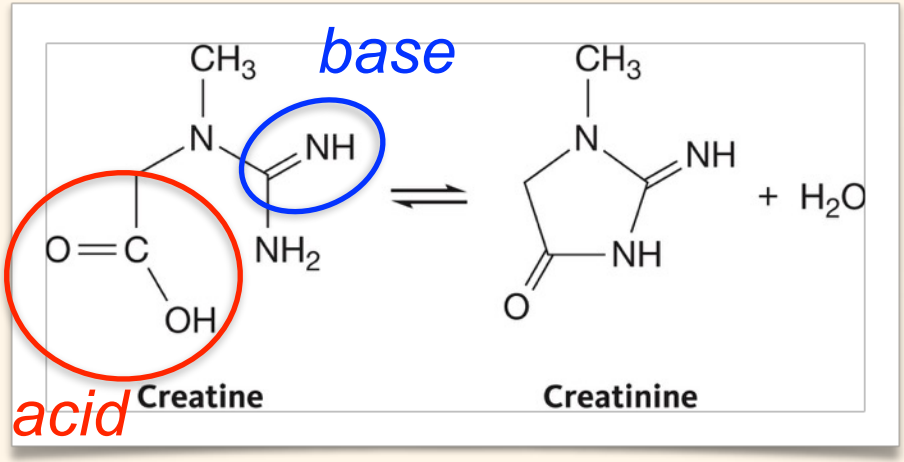

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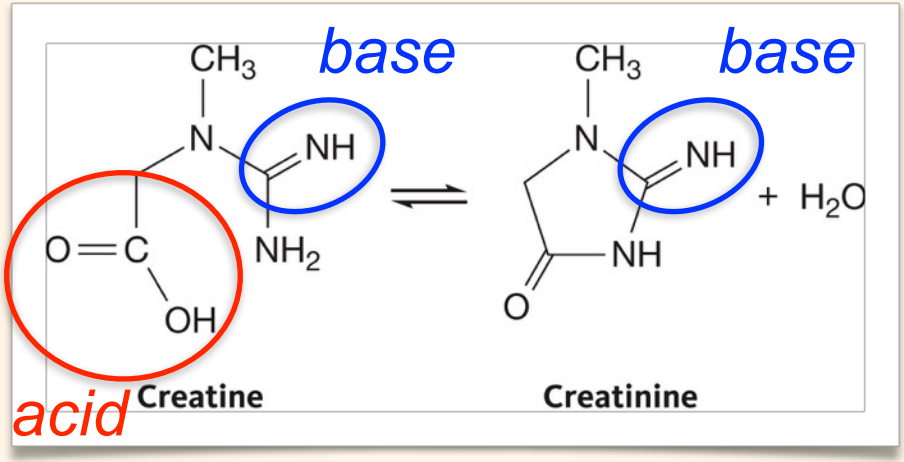
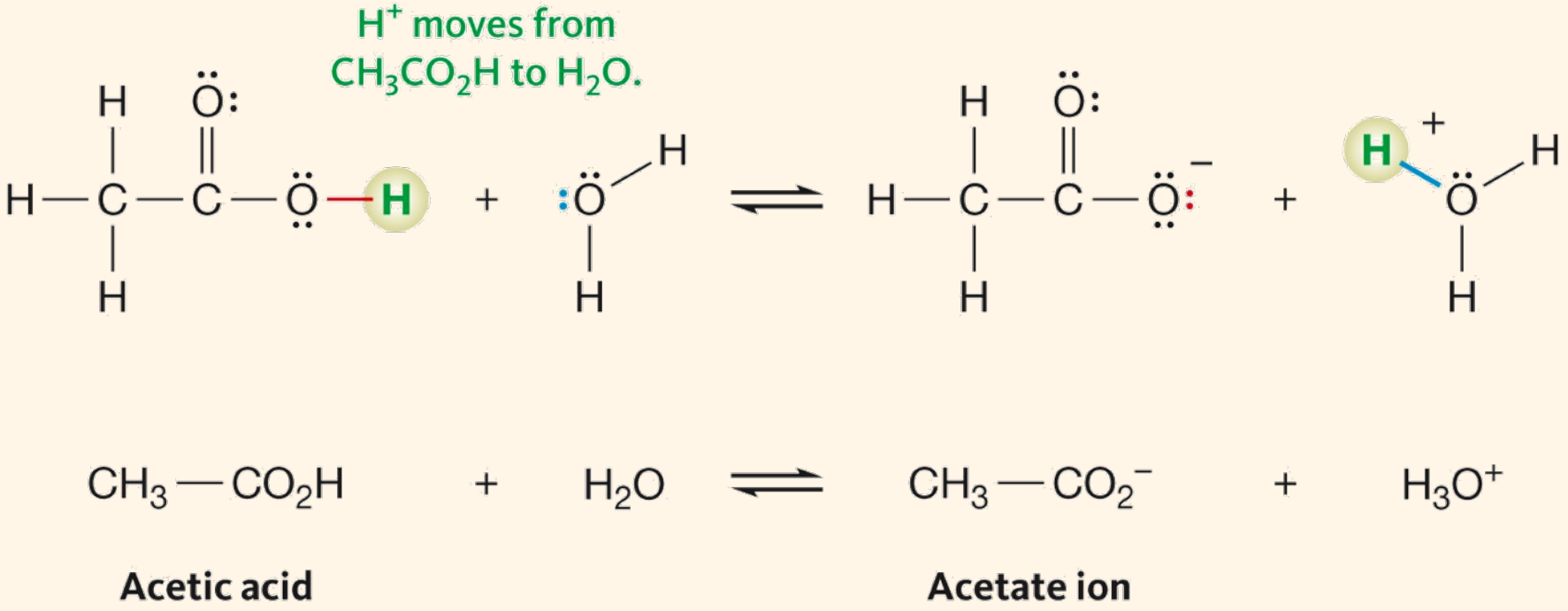


12.1 Reactions of Organic Acids

- When dissolved in water, **carboxylic acids**, like all acid, can donate a proton (H^+) to a water molecule.



  - We use double arrows because they are weak acids.

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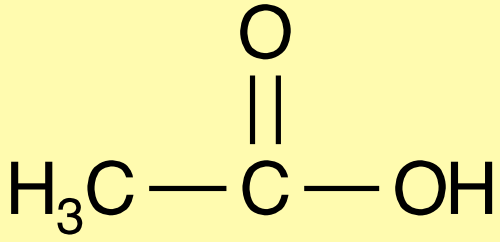
Question:

What is the IUPAC name for **acetic acid**?



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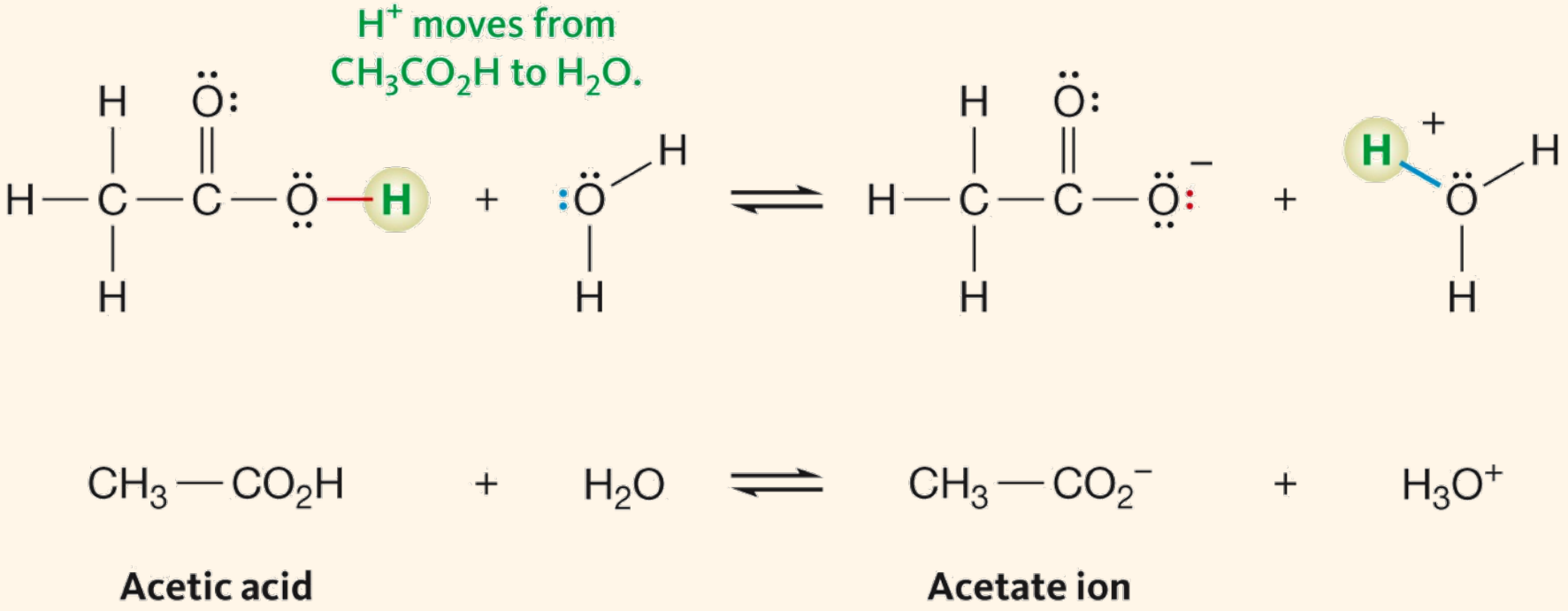

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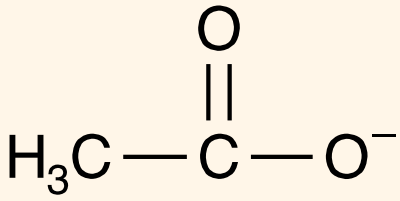
Carboxylic Acids React with Bases

- When a carboxylic acid loses a proton it becomes negatively charged.
  - We then call it a **carboxylate ion**.
  - When acetic acid loses a proton we call it an **acetate ion**.
  - The IUPAC name for an acetate ion is an **ethanoate ion**.



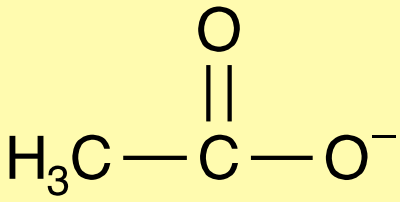
acetate ion

Carboxylic Acids React with Bases

- When a carboxylic acid loses a proton it becomes negatively charged.

Question:

What non-covalent interactions can an acetate ion have with other acetate ions?



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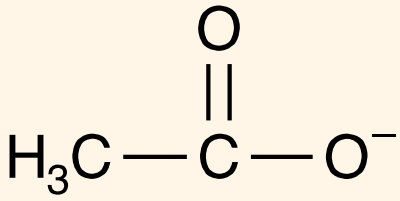
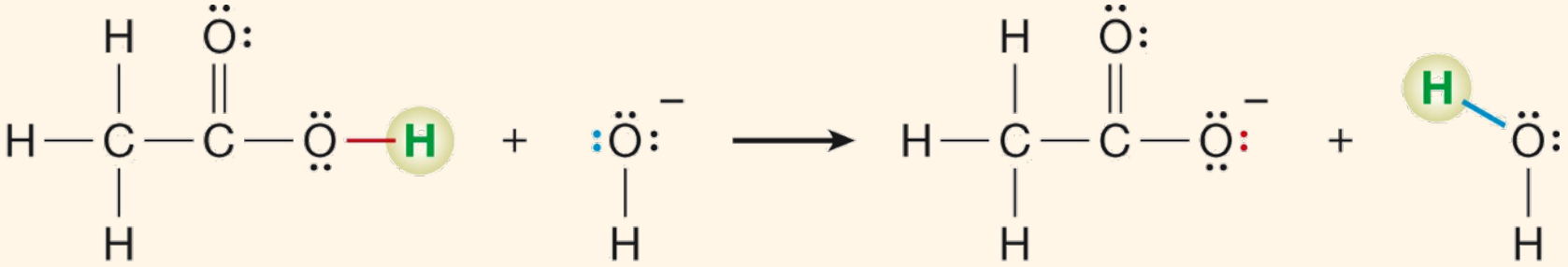


acetate ion

Carboxylic Acids React with Bases

- Whenever a carboxylic acid reacts with a base, one of the products is the conjugate base of the original acid, which is a carboxylate ion.

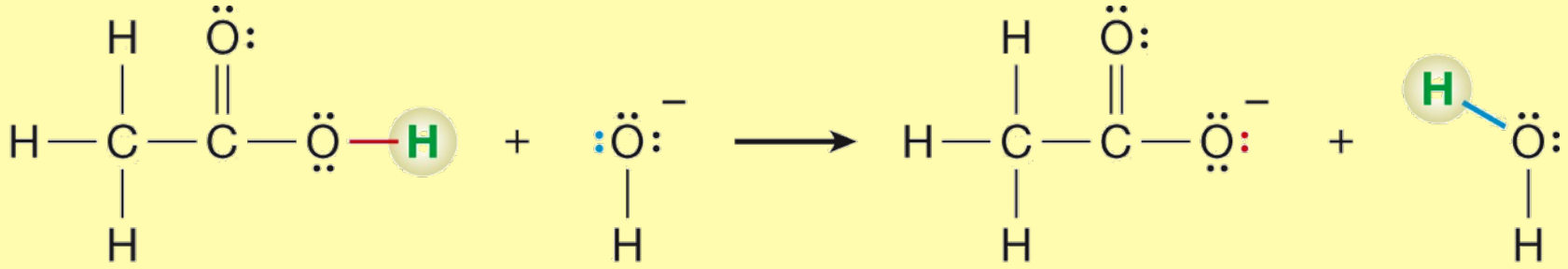


$$CH_3—CO_2H + OH^- \longrightarrow CH_3—CO_2^- + H_2O$$

Carboxylic Acids React with Bases

- Question:

  Write a **total ionic equation** for this reaction:



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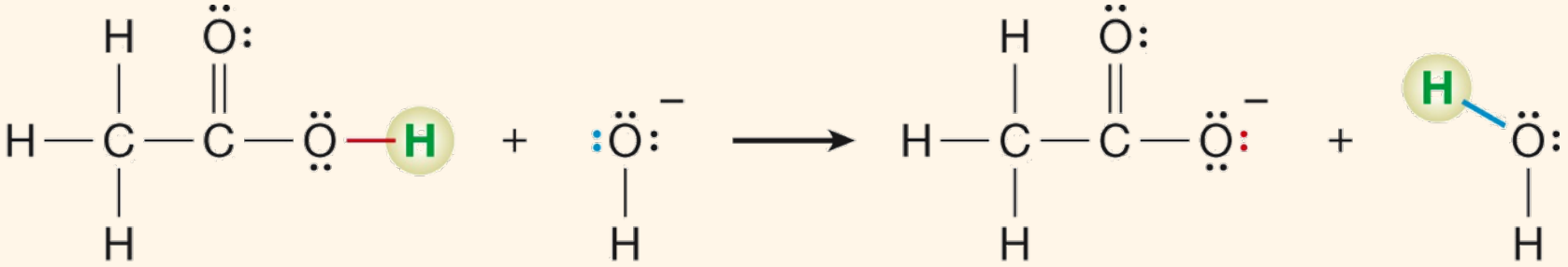

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Carboxylate Ions

- The names of carboxylate ions are derived from the names of the original acids.
  - To name a carboxylate ion, remove –*ic acid* from the name of the acid and add the suffix –*ate*.
  - The organic ions in such salts are often written as if they are molecular formulas.
  - The carboxylate functional group is an ion, so it is strongly attracted to water.
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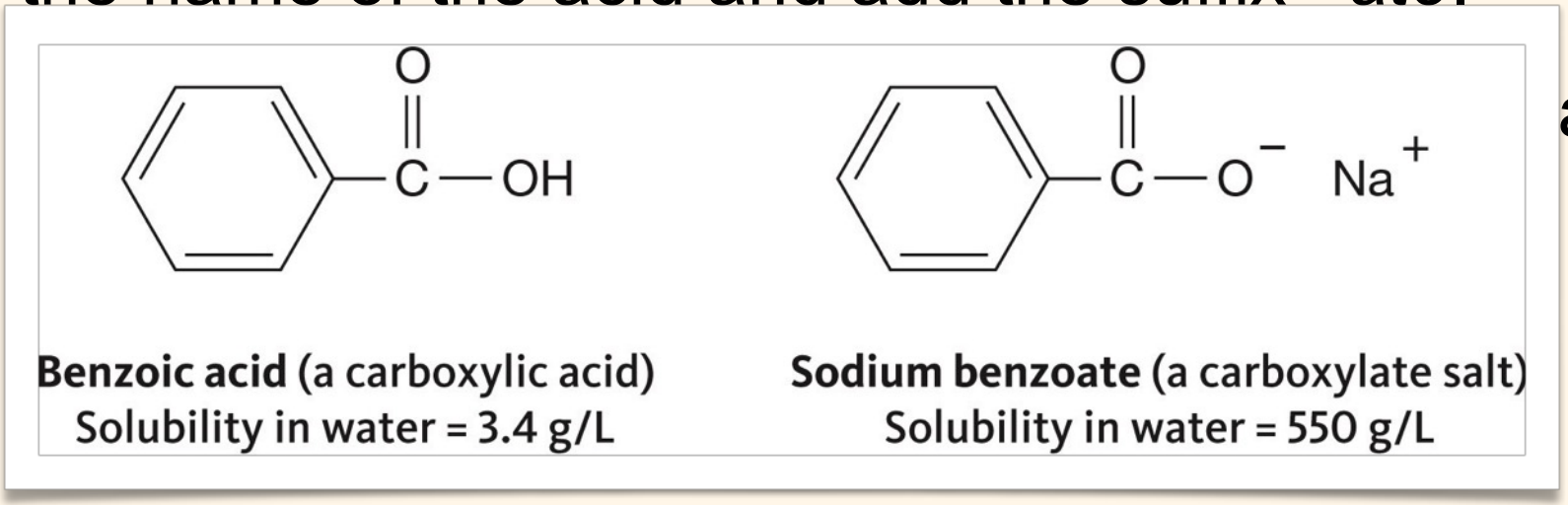

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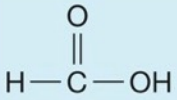
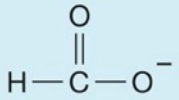
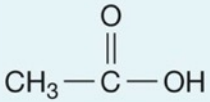
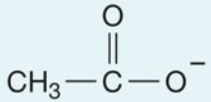
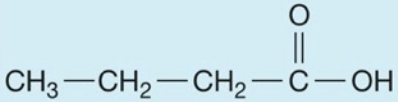
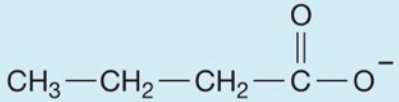
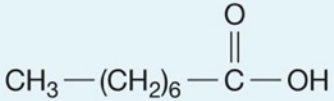
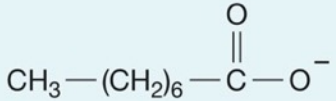
The Structures of Some Carboxylic Acids and Their Conjugate Bases

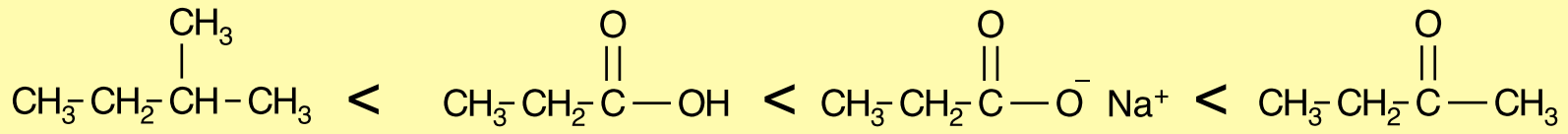
TABLE 12.1 The Structures of Some Carboxylic Acids and Their Conjugate Bases

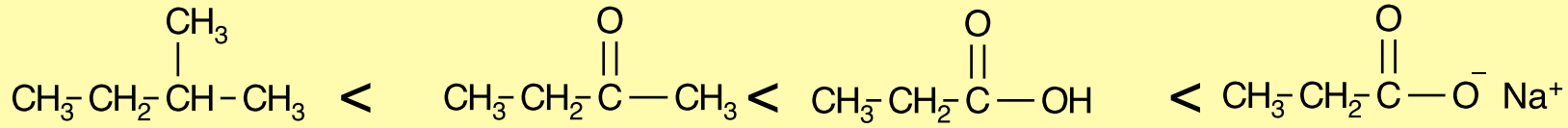
Acid	Name of Acid	Conjugate Base	Name of Conjugate Base
	Formic acid (methanoic acid)		Form*ate* ion (methano*ate* ion)
	Acetic acid (ethanoic acid)		Acet*ate* ion (ethano*ate* ion)
	Butanoic acid		Butano*ate* ion
	Octanoic acid		Octano*ate* ion

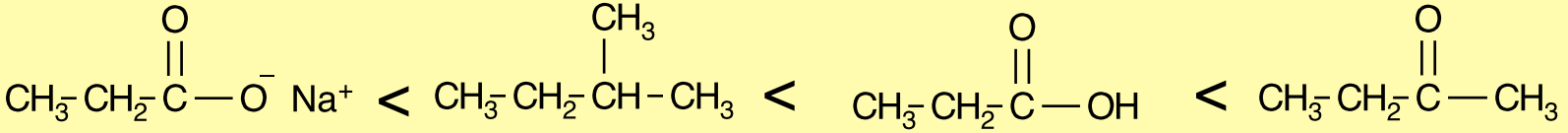
Try It

Question:

Which is the most likely correct ranking by melting points?

A. 

B. 

C. 

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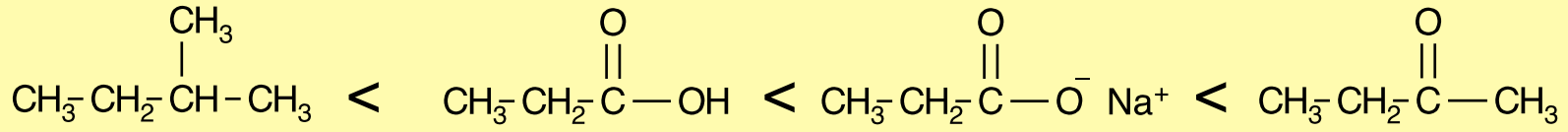
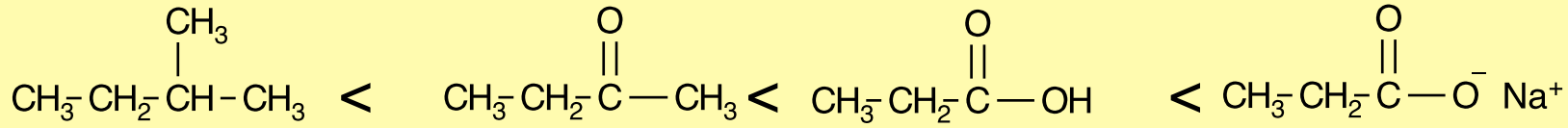
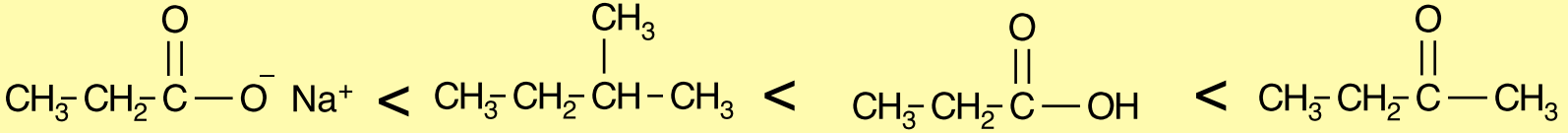
A. 

B. 

C. 

What are the IUPAC names for these compounds?

Reactions of Thiols and Phenols

Question:

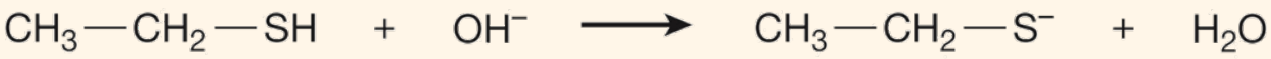
Thiols and phenols are also weak acids. Write a chemical equation for the reaction of these acids with sodium hydroxide.

Reactions of Thiols and Phenols

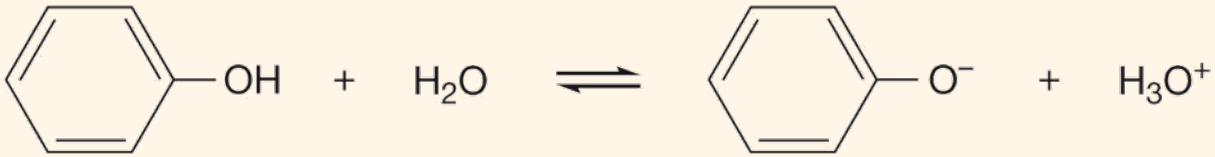
- Thiols and phenols are also weak acids

Thiol + water:

Thiol + hydroxide ion:



Phenol + water:



Phenol + hydroxide ion:

12.2 Decarboxylation Reactions

- Carboxylic acids can lose carbon dioxide in a decarboxylation reaction. Decarboxylation reactions only occur if there is another functional group on one of the two carbons closest to the acid group (*alpha* and *beta* carbon atoms)
- Decarboxylation is often combined with oxidation in biological reactions and is referred to as an oxidative decarboxylation. This reaction requires a carbonyl group on the alpha carbon. The other reactants are NAD^+ and a thiol with a thioester product.

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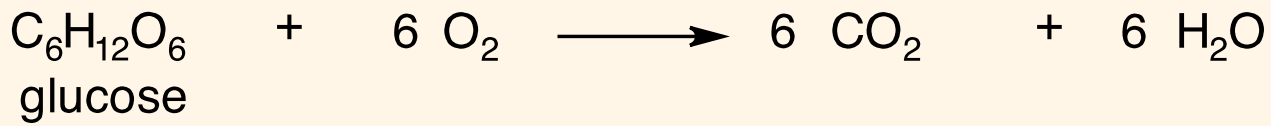

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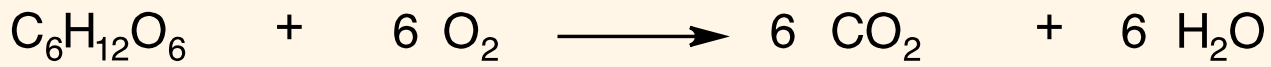
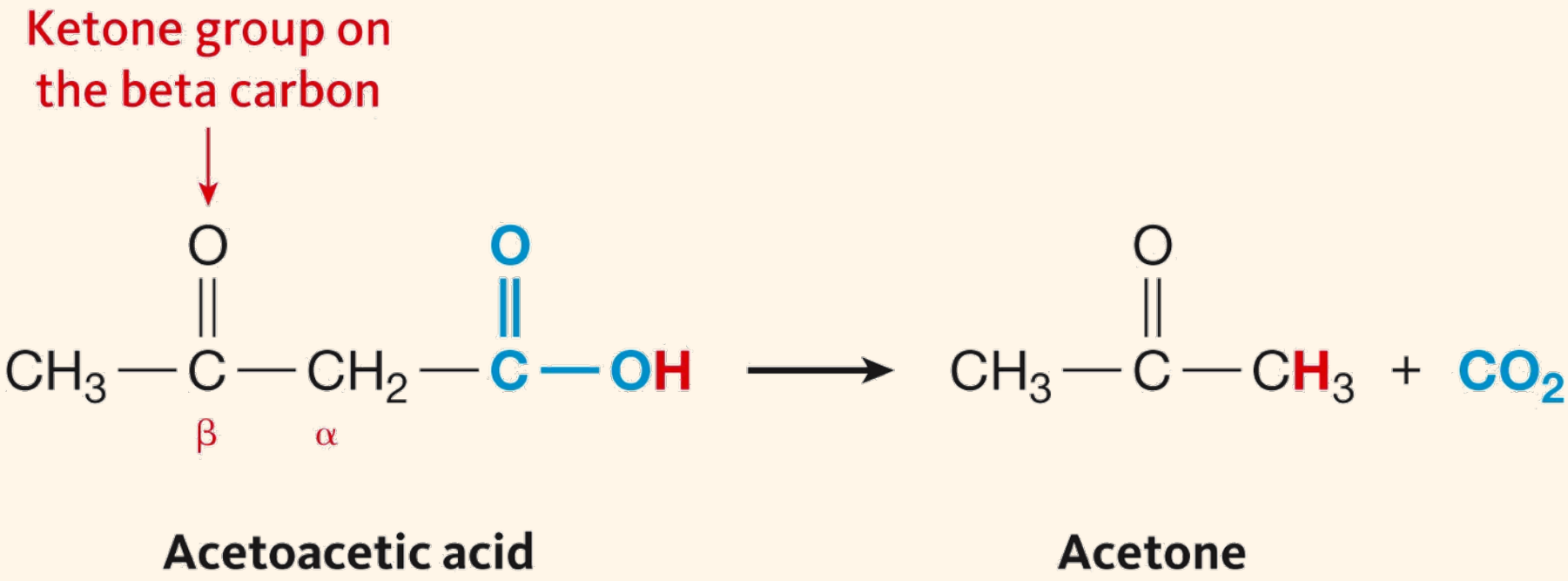


The "combustion" of glucose

A Decarboxylation Reaction

- Ketone bodies



Oxidative Decarboxylation

- Decarboxylation reactions in **glycolysis** and **citric acid cycle** pathways
  - oxidative decarboxylation of pyruvate
  - oxidative decarboxylation of isocitrate
  - oxidative decarboxylation of α-ketoglutarate
- Decarboxylation reaction in **alcoholic fermentation** pathway

Comparison of the Two Types of Decarboxylation Reactions

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Decarboxylation	Oxidative Decarboxylation
The reaction is not an oxidation (no NAD^+ is required).	The reaction requires NAD^+ to remove hydrogen atoms.
No thiol is required.	The reaction requires a thiol (usually coenzyme A).
The carboxylic acid usually has a ketone group on the β-carbon.	The carboxylic acid has a ketone group on the α-carbon.
The product is a ketone.	The product is a thioester.

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12.3 Amines

- Nitrogen has five valence electrons, so it forms three covalent bonds.
- Nitrogen can also form four covalent bonds, but it will be a positively charged ion.
- If one or more of the groups on nitrogen is an alkyl group, it is an organic compound called an amine.
- Amines can be classified as primary, secondary, or tertiary based on the number of carbon atoms bonded to the nitrogen atom.

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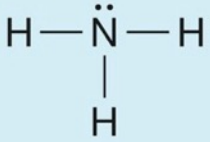
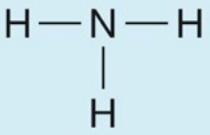
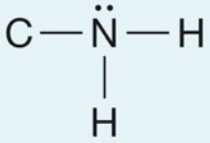
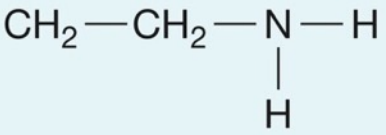
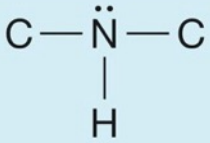
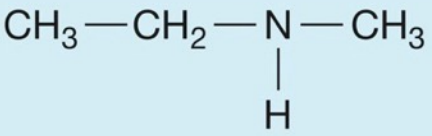
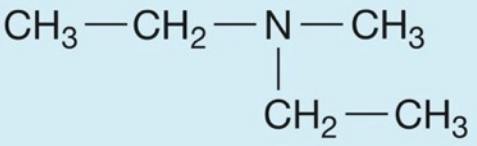
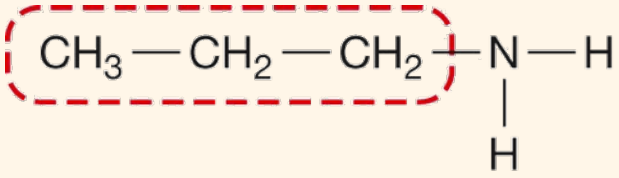
The Classes of Amines

TABLE 12.3 The Classes of Amines

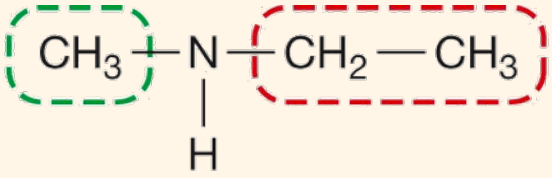
Class	Atoms Bonded to Nitrogen	General Structure	Example
Ammonia (not an organic compound)	3 hydrogen atoms		
Primary amine	**1 carbon atom** + 2 hydrogen atoms		
Secondary amine	**2 carbon atoms** + 1 hydrogen atom		
Tertiary amine	**3 carbon atoms**		

Naming Amines

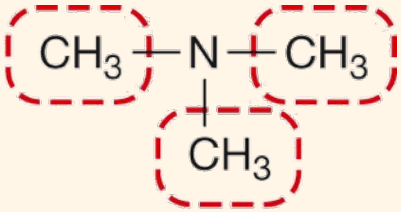
- Simple amines are named by listing each alkyl group alphabetically that is bonded to the nitrogen followed by the suffix –*amine*.
- If there are two or three identical groups, the prefixes *di-* and *tri-* are used rather than writing the name of the alkyl group several times.



Propylamine



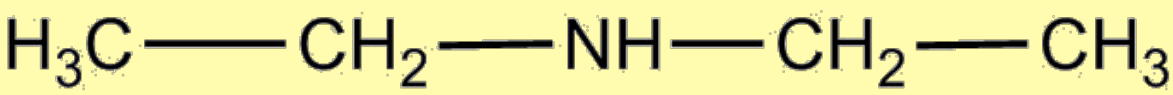
Ethylmethylamine



Trimethylamine

Try It!

Clicker Question:

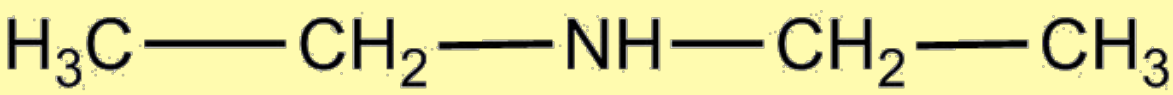


The amine shown above is a

A. primary amine
B. secondary amine
C. tertiary amine
D. quaternary amine

Try It!

Clicker Question:



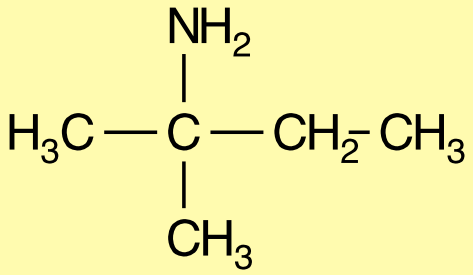
The amine shown above is a

A. primary amine
B. secondary amine
C. tertiary amine
D. quaternary amine

What is the name for this amine?

Try It!

Clicker Question:

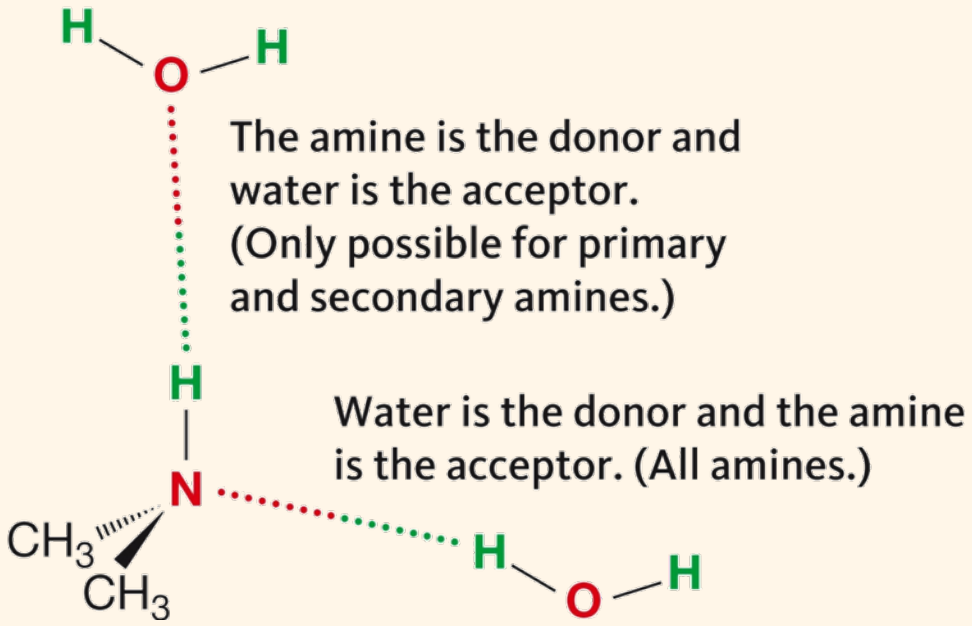


The amine shown above is a

A. primary amine
B. secondary amine
C. tertiary amine
D. quaternary amine

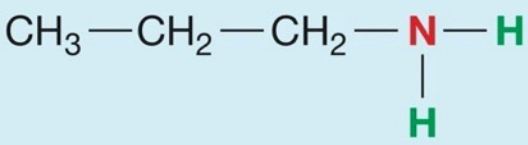
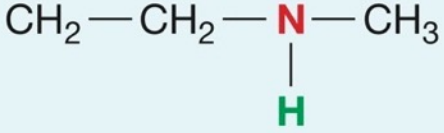
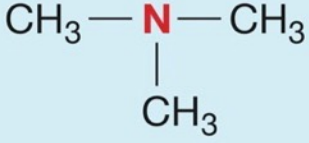
Amines and Hydrogen Bonding

- Primary and secondary amines form hydrogen bonds. The nitrogen of a tertiary amine can act as a hydrogen bond acceptor.
- As a result many amines dissolve well in water.



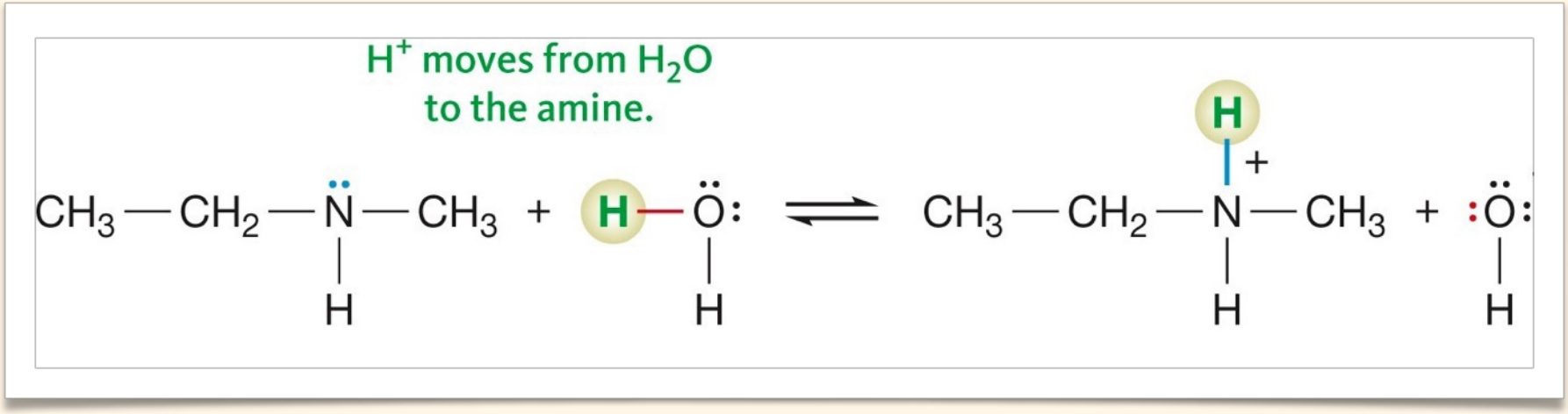
The Effect of Hydrogen Bonding on the Boiling Point of an Amine

TABLE 12.4 The effect of hydrogen bonding on the boiling point of an amine

Compound	Structure	Boiling Point
Propylamine (a primary amine: hydrogen bonding occurs between molecules)		48°C
Ethylmethylamine (a secondary amine: hydrogen bonding occurs between molecules)		37°C
Trimethylamine (a tertiary amine: no hydrogen bonding is possible)		3°C
Butane (an alkane: no hydrogen bonding is possible)		−1°C

12.4 Acid-Base Reactions of Amines

- Most amines are bases because they can act as proton acceptors.
- Amines are weak bases, producing only a small concentration of hydroxide ions when they dissolve in water.
- Amines can react with any source of H^+.



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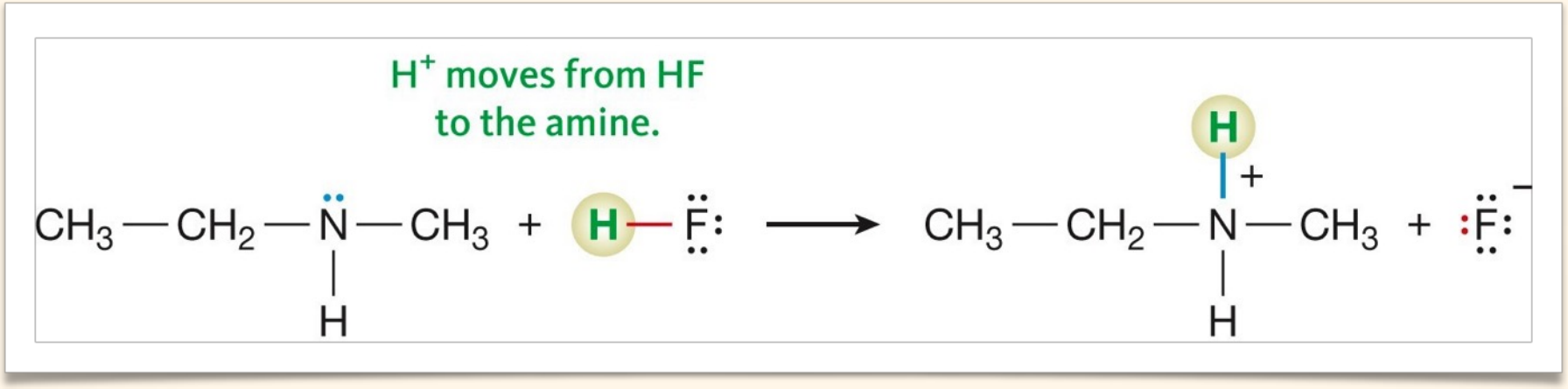
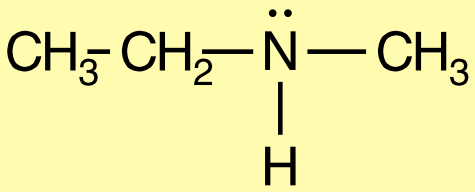


Try It!

Clicker Question:



What class of amine was shown on the previous slide?

A. primary amine

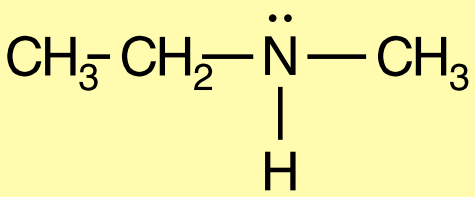
B. secondary amine

C. tertiary amine

D. quaternary amine

Try It!

Clicker Question:



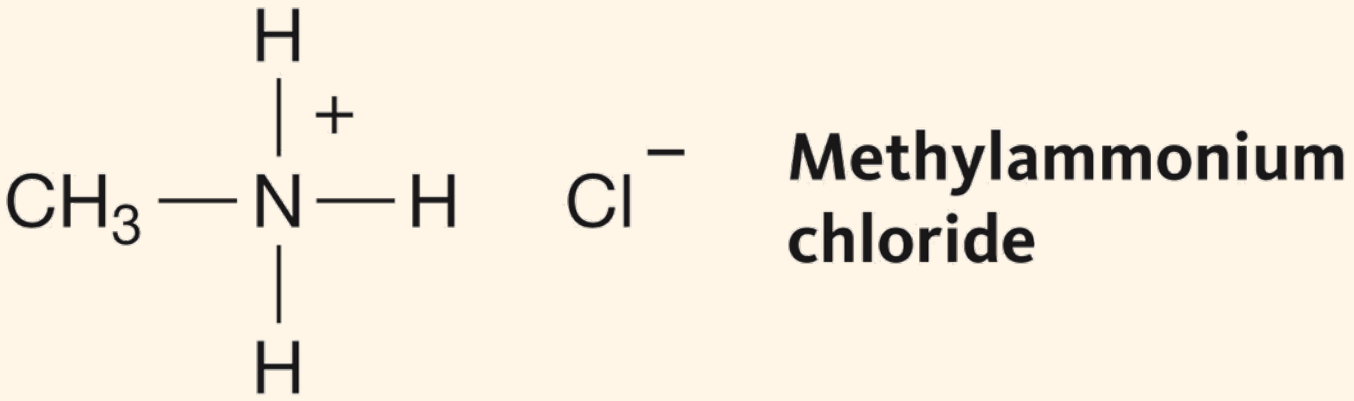
What is the name of this amine?

What class of amine was shown on the previous slide?

A. primary amine
B. secondary amine
C. tertiary amine
D. quaternary amine

Conjugate Acids of Amines

- The conjugate acids of amines are called alkylammonium ions.
- Alkylammonium ions can combine with negative ions to form salts.
- As with all ionic compounds, we name the cation first, followed by the anion.



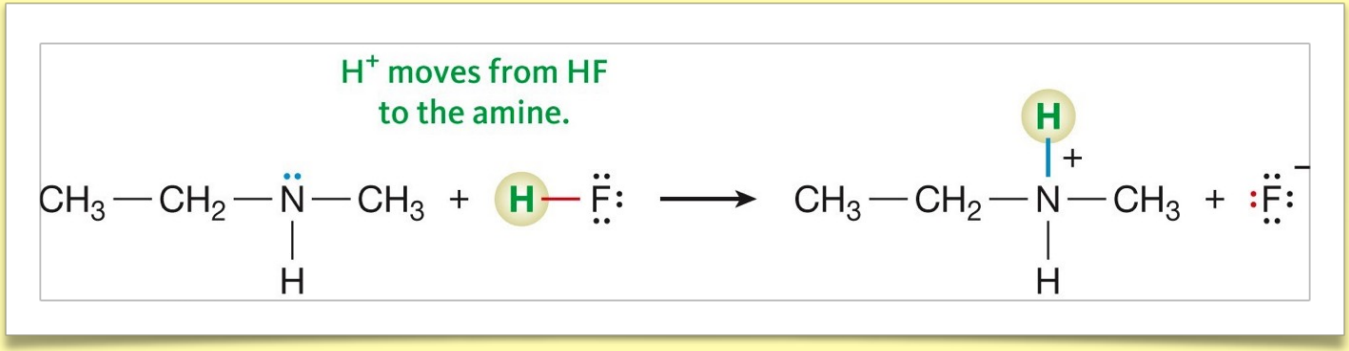
Try It!

Question:

What is the name of the product in the above reaction?

Try It!

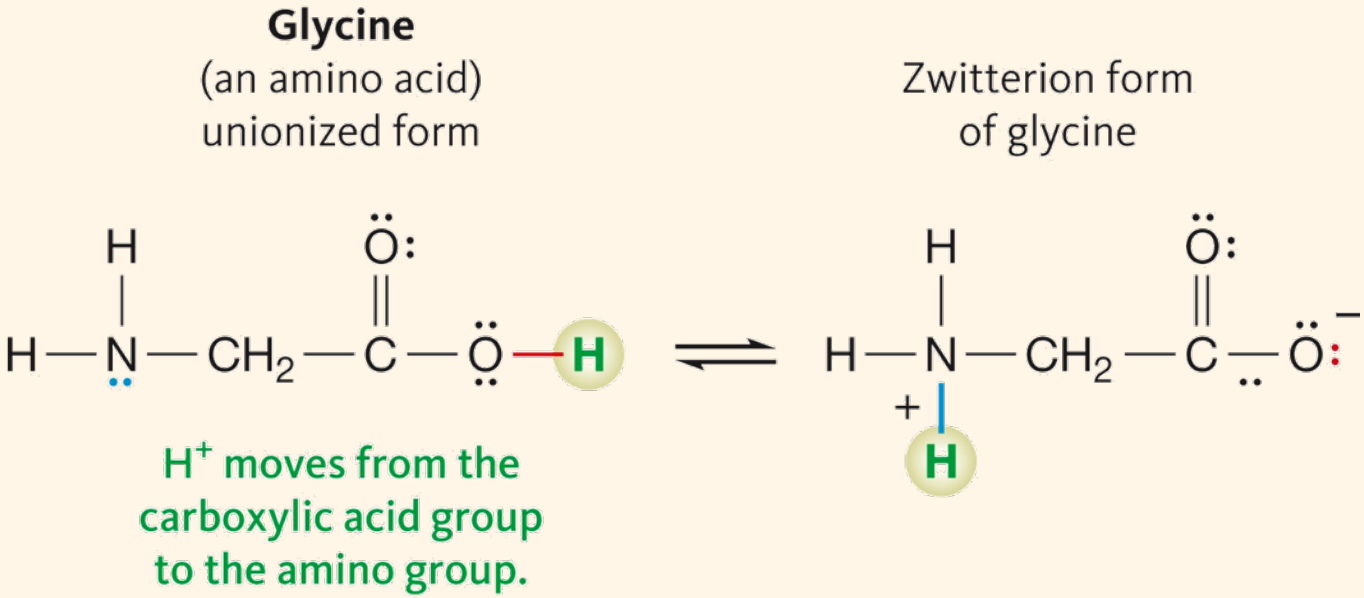
Question:



What is the name of the product in the above reaction?

Amino Acids

- Substances contianing **both** an amino group and a carboxylic acid group within the same molecule are *amino acids*.
- Amino acids are used to make **peptides** and **proteins**
- The amine group and carboxylic acid groups are both ionized in water giving these compounds both both a positive and a negative charge. Such molecules are called zwitterions.



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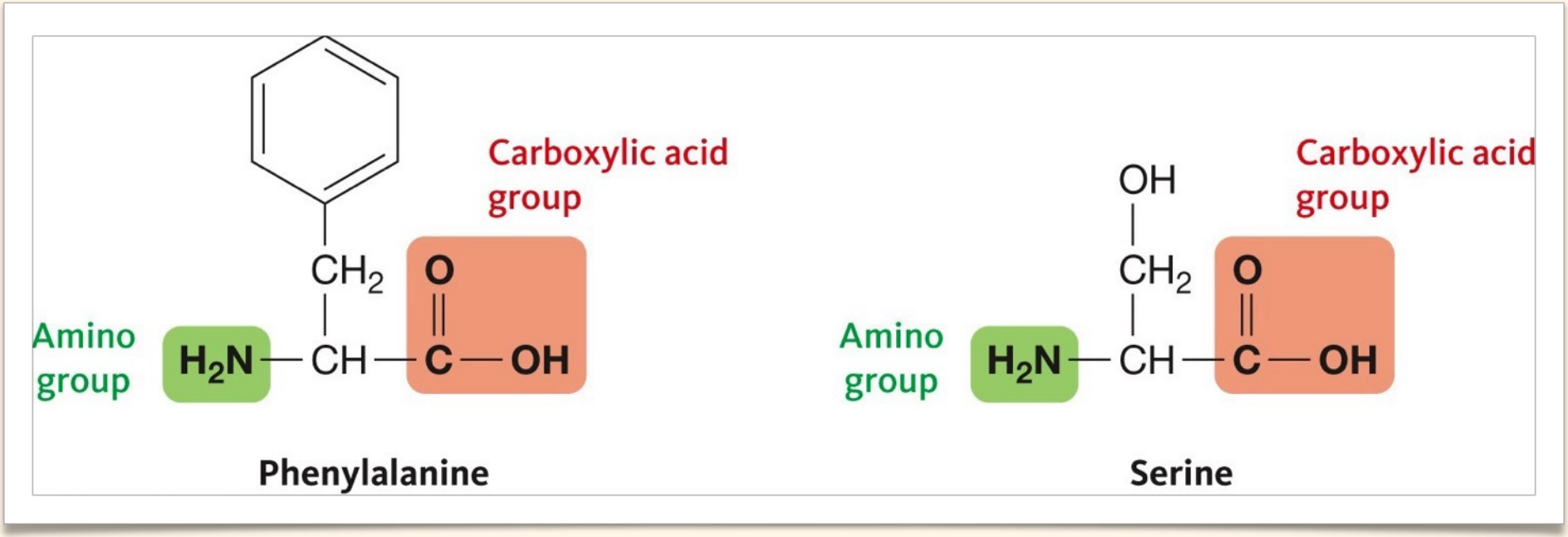

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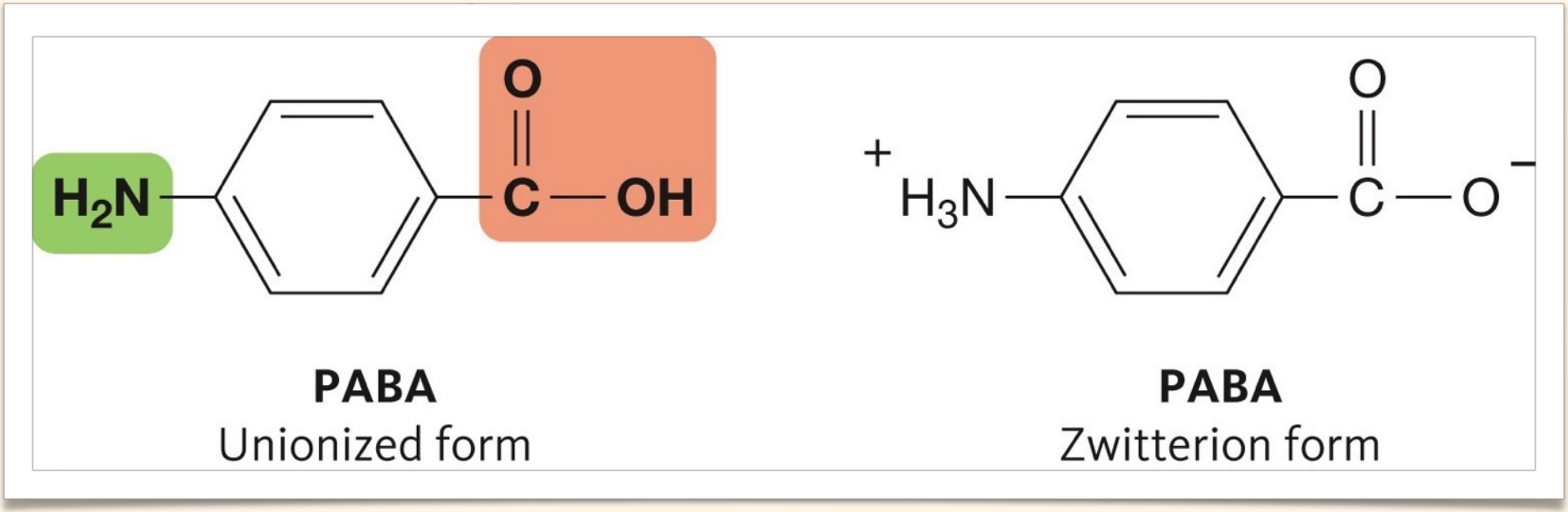
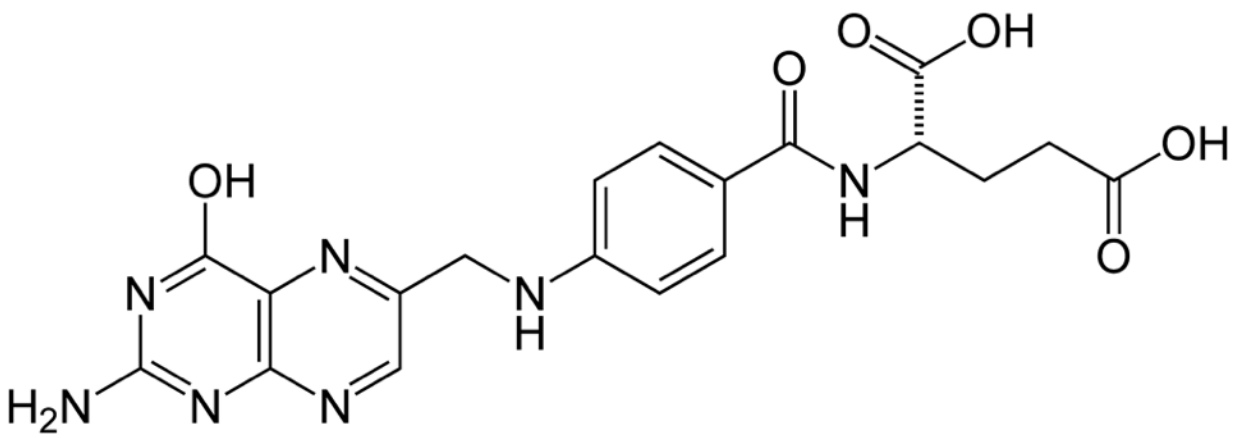
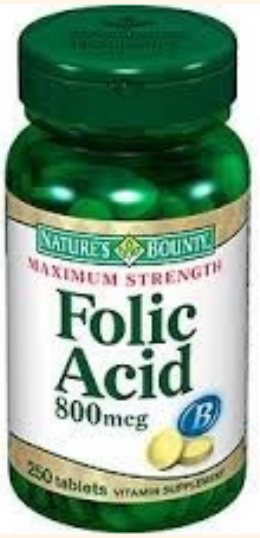
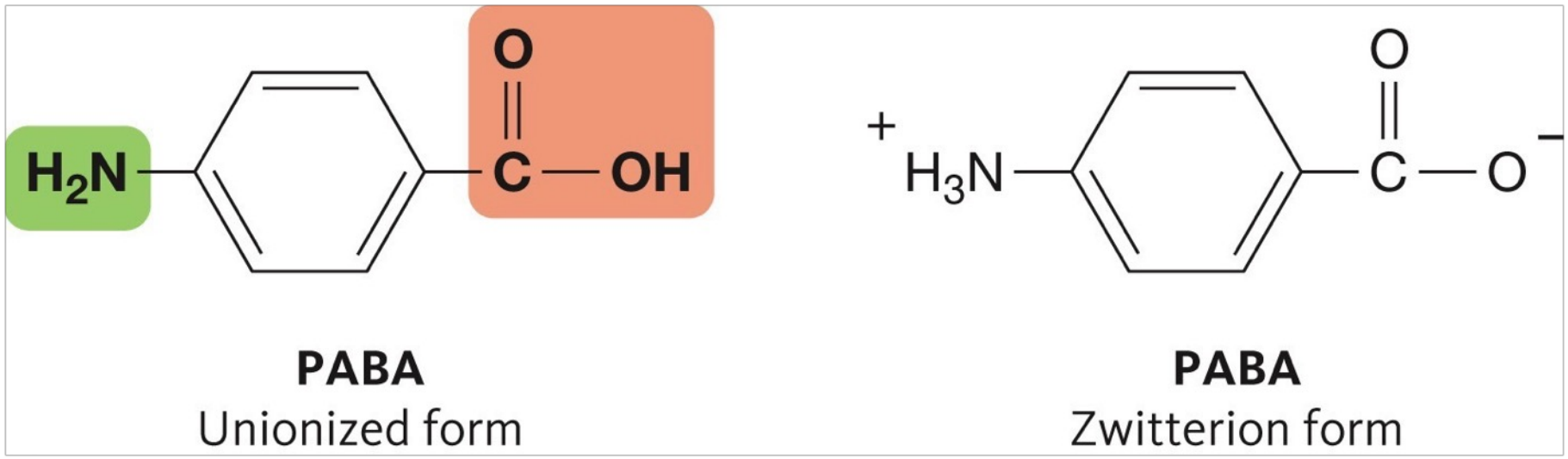


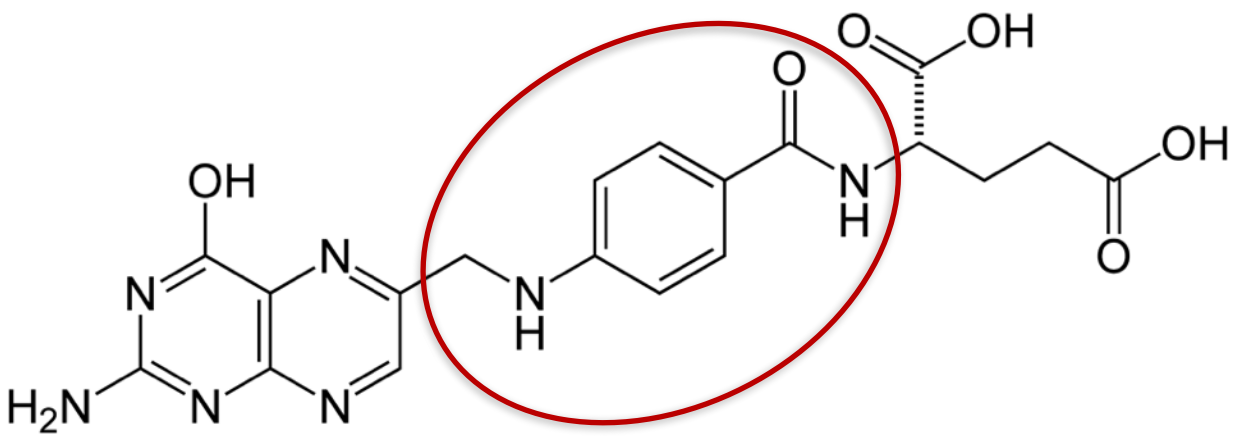
Amino Acids

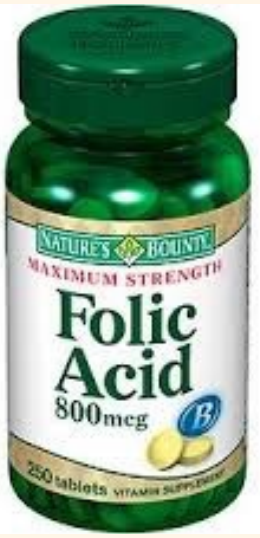

OH
N
N
N
N
H
O
OH
O
N
H
OH
O
H_2N


NATURE'S BOUNTY
MAXIMUM STRENGTH
Folic Acid
800mcg
250 tablets


H_2N
O
C
OH
PABA
Unionized form
+
H_3N
O
C
O
−
PABA
Zwitterion form

Amino Acids


OH
N
N
N
N
H
O
OH
O
N
H
OH
O
H_2N


NATURE'S BOUNTY
MAXIMUM STRENGTH
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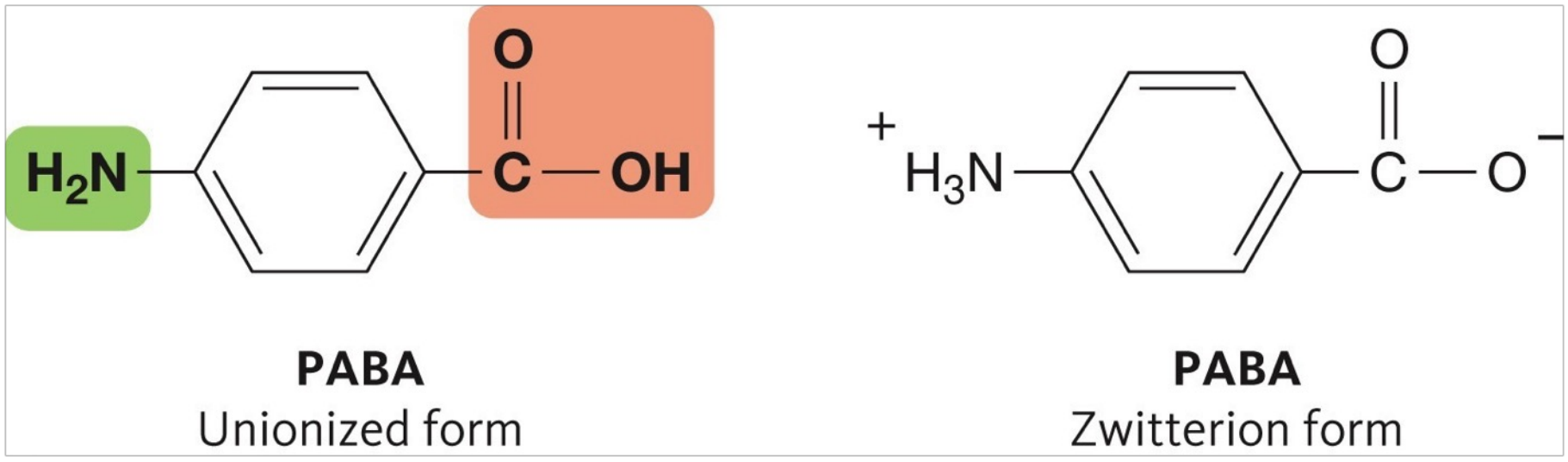
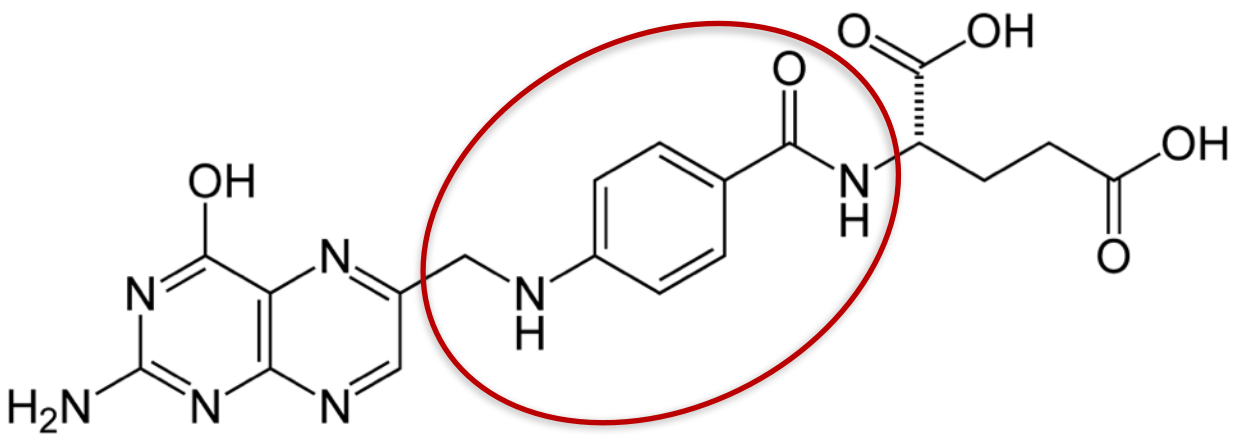
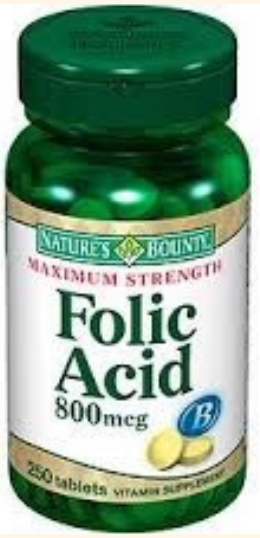
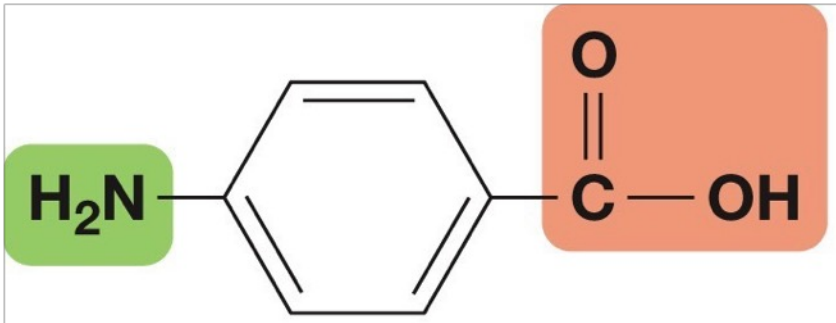

H_2N
O
C
OH
PABA
Unionized form
+
H_3N
O
C
O
−
PABA
Zwitterion form

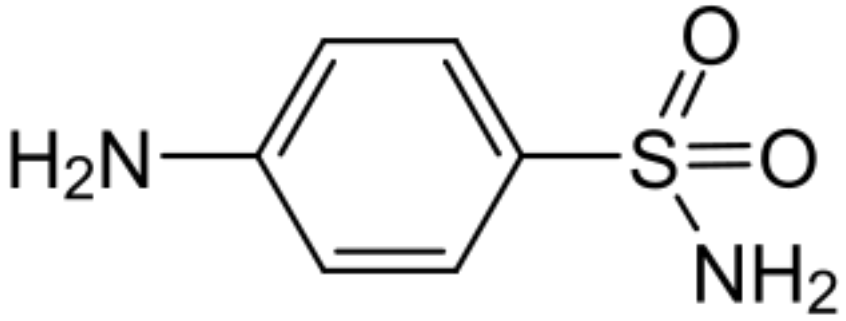
Amino Acids







PABA
Unionized form



Sulfanilamide
(a sulfa drug antibiotic)

Amino Acids

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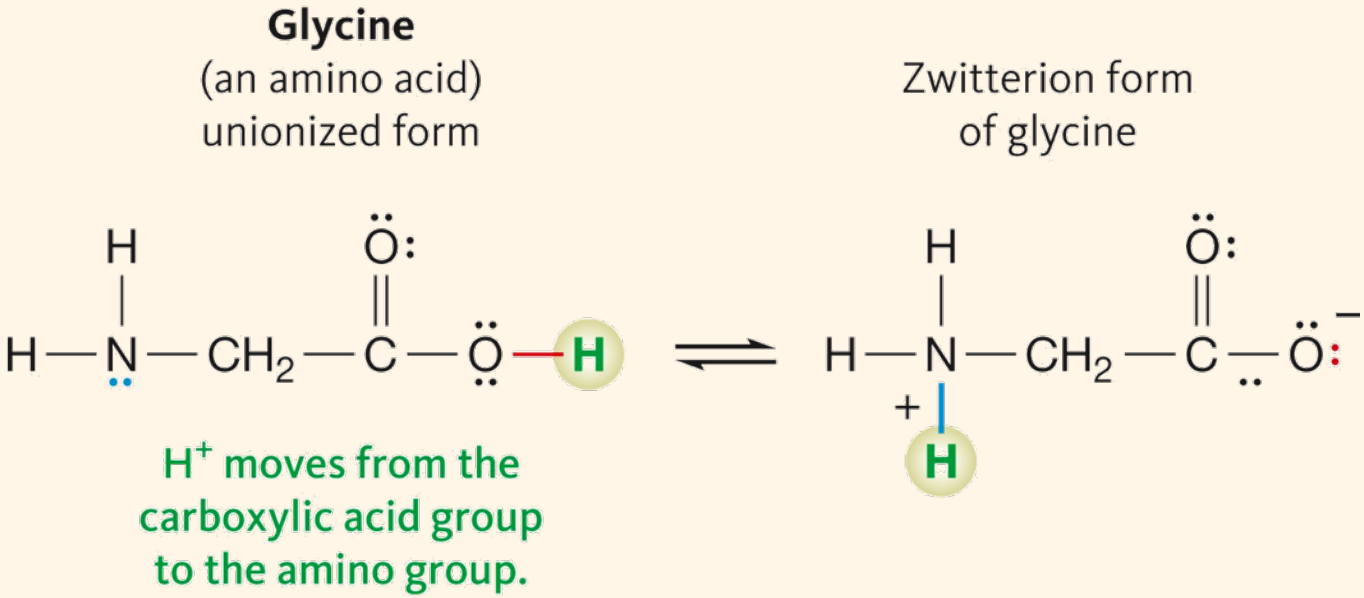
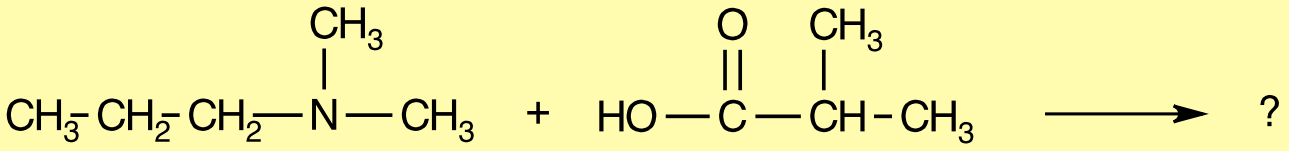
- Amino acids are used to make **peptides** and **proteins**
- The amine group and carboxylic acid groups are both ionized in water giving these compounds both both a positive and a negative charge. Such molecules are called zwitterions.



Try It!

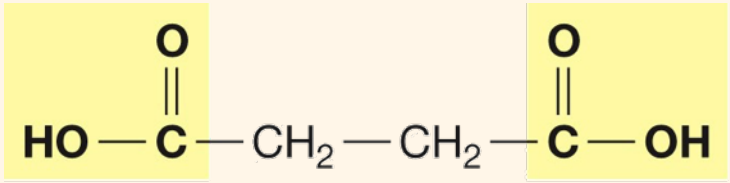
Question:



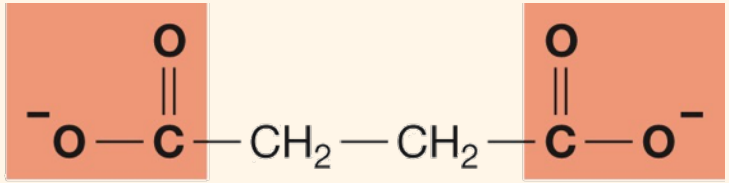
Complete the reaction equation shown above and name both the reactants and product of this reaction?

12.5 The Physiological Behavior of Organic Acids and Bases

- At *pH* 7, carboxylic acids are in their conjugate base forms.
- Many organic acids that are important in biochemistry contain two or more carboxylic acid functional groups. Most of the fluids in our bodies have *pH's* around 7, so these groups are usually present as carboxylate ions.



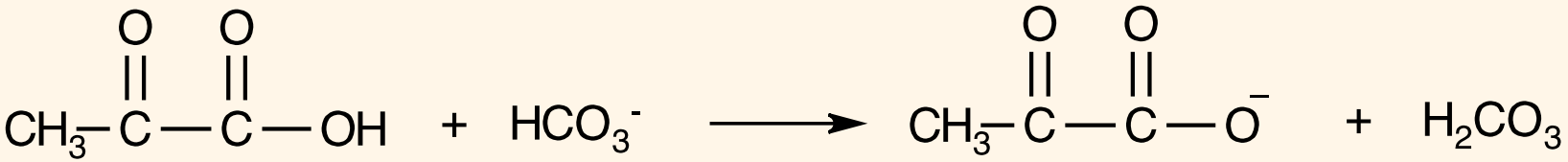
Succinic acid



Succinate ion
The dominant form at physiological pH

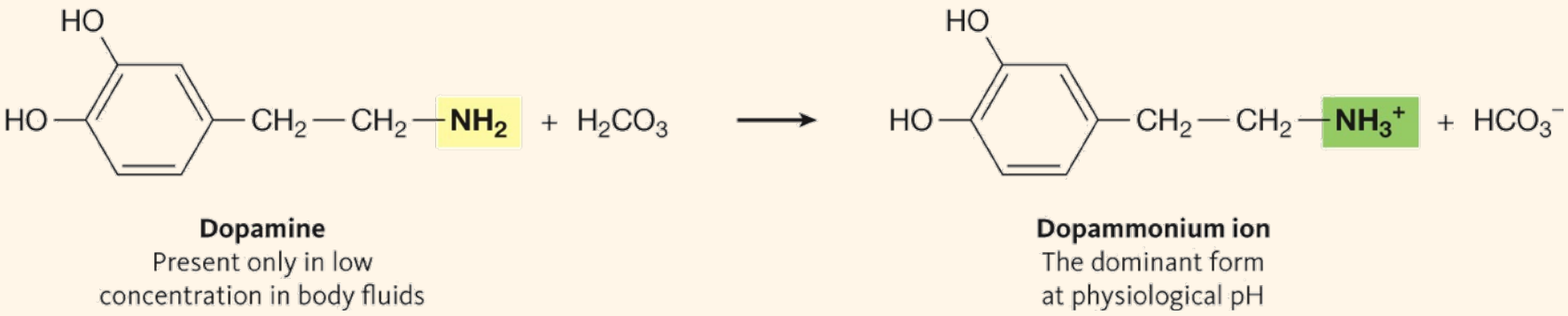
Amines and pH

- As we learned in Unit 4, are bodies have buffers that help to resist changes in *pH* when acids are formed during metabolism.
- Active muscles convert glucose to lactic acid, which is released into the blood. There this acid can be neutralized by bicarbonate ions (HCO_3^-).



Amines and pH

- Likewise, amines at *pH 7* are in their conjugate acid form.
- Dopamine is a neurotransmitter that affects many aspects of our nervous system. The amine group in dopamine is neutralized by carbonic acid in body fluids.

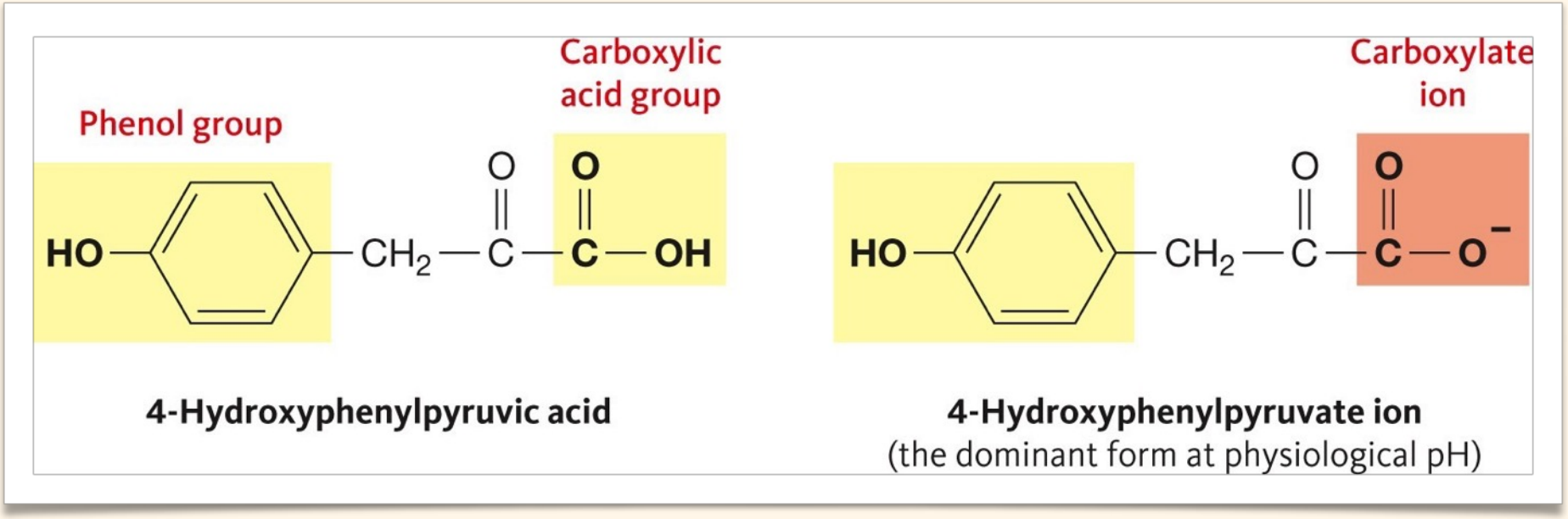


Dopamine
Present only in low concentration in body fluids

Dopammonium ion
The dominant form at physiological pH

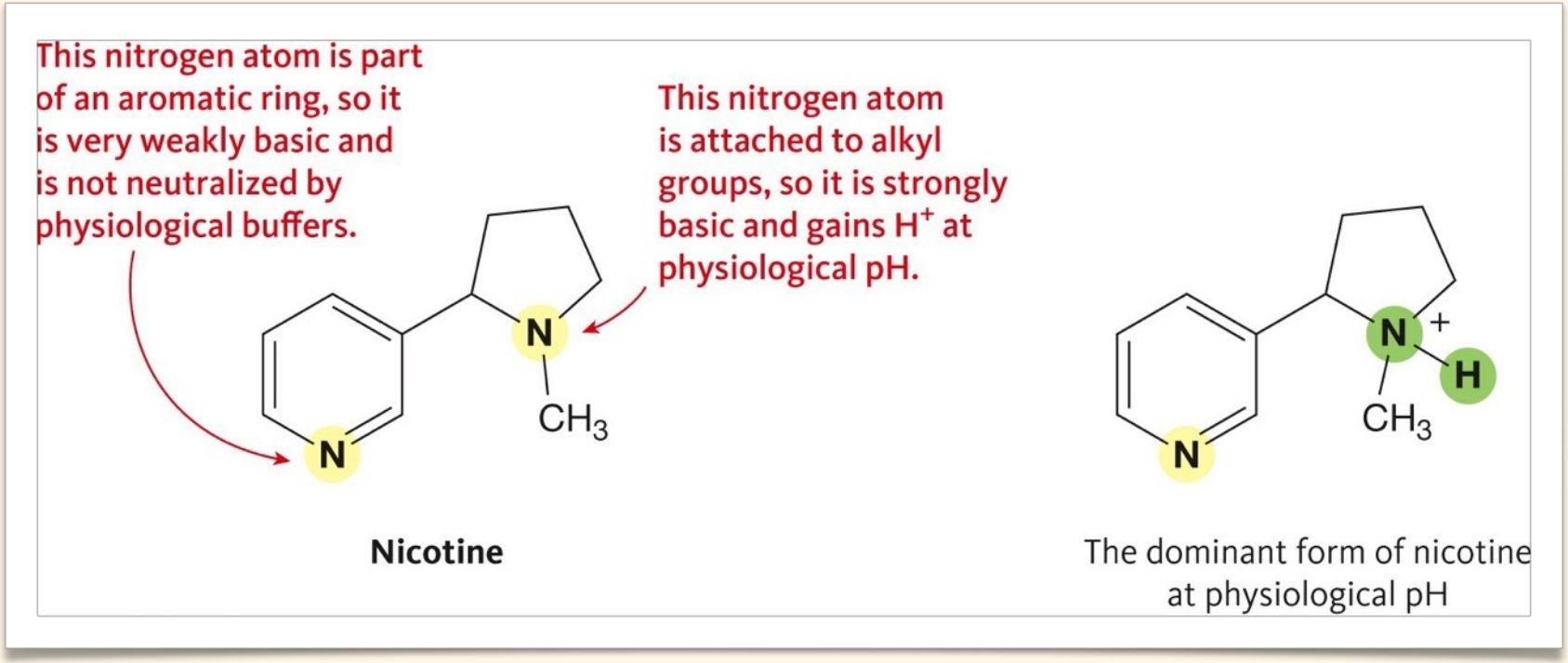
Amines and pH

- Even though phenols and thiols are weak acids, they have pK_a's that are greater than 7 and therefore remain in their acid form at *pH* 7.



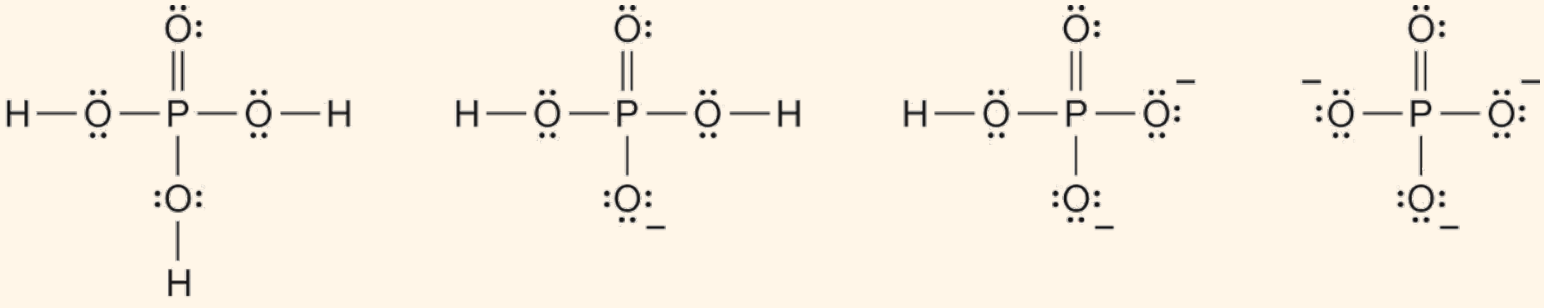
Amines and pH

- Aromatic amines are also very weak and are not converted to their conjugate acid forms a physiological *pH* values.



Organic Phosphates Form Buffers

- As we learned in Unit 4, Phosphoric acid is a triprotic acid.
- The dihydrogen phosphate ion ($H_2PO_4^-$) and the mono hydrogen phosphate ion (HPO_4^{2-}) are the forms that are predominant at *pH* 7.
- These ions are important in buffering the intracellular *pH*.



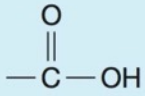
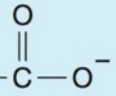
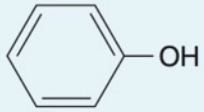
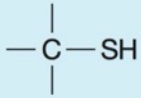
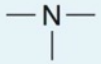
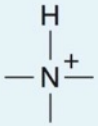
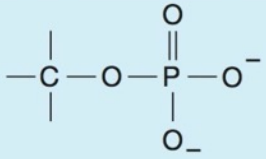
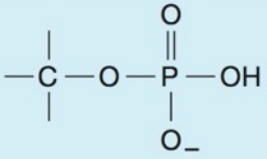
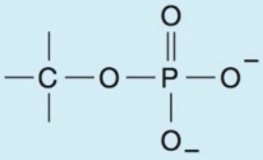
H_3PO_4
(phosphoric acid)
Not present in significant amounts at pH 7

$H_2PO_4^-$ **HPO_4^{2-}**
Predominant ions at pH 7

PO_4^{3-}
(phosphate ion)
Not present in significant amounts at pH 7

Summary of Organic Acids and Bases Under Physiological Conditions

TABLE 12.5 Summary of Organic Acids and Bases under Physiological Conditions

Functional Group	Structure of Functional Group	Structure at Physiological pH (around 7)
Carboxylic acid		
Phenol		Same as original phenol
Thiol		Same as original thiol
Amine (if the nitrogen atom is not attached to or part of an aromatic ring)		
Organic phosphate		 and 

Next Up

- Unit 9: Condensation and Hydrolysis Reactions
  - Chapter 13 in Armstrong
  - Unit 9 Assignments due 31. March (deadline 7. April)
- Exam II on 2. April
  - Will cover Units 5 - 8