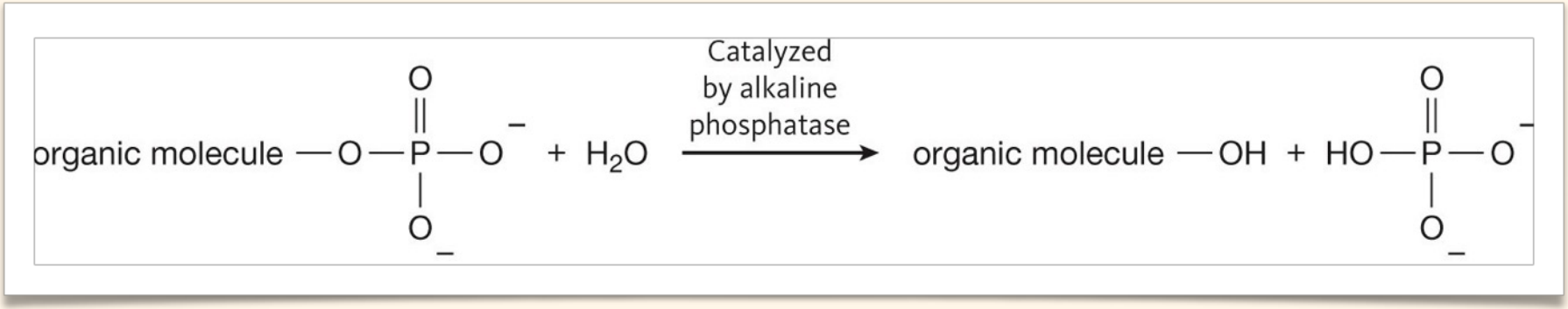
Chem 150, Spring 2015

Unit 9 - Condensation and Hydrolysis Reactions

Introduction

- The levels of certain enzymes in the blood can be used to diagnose various health-related issues.
  - For example, elevated levels of the enzyme alkaline phosphatase is an indication of a bone injury.



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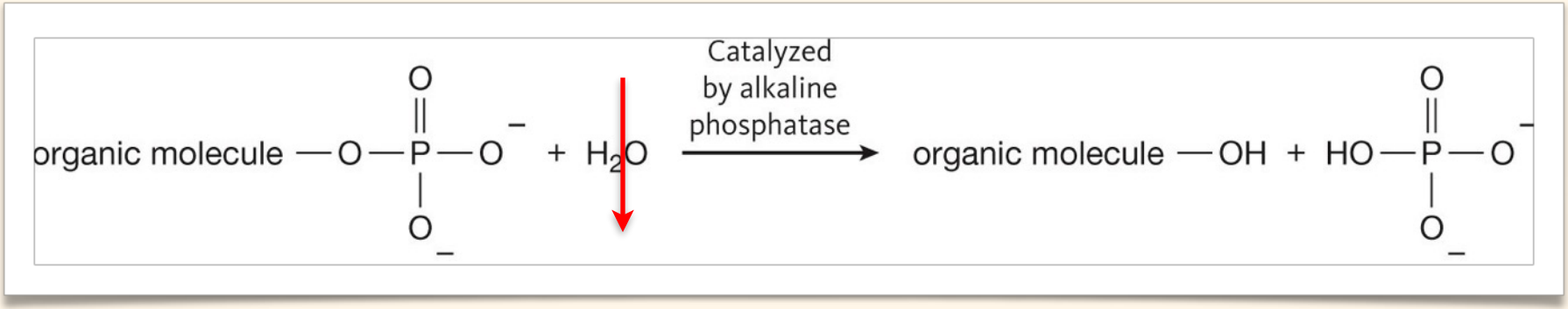

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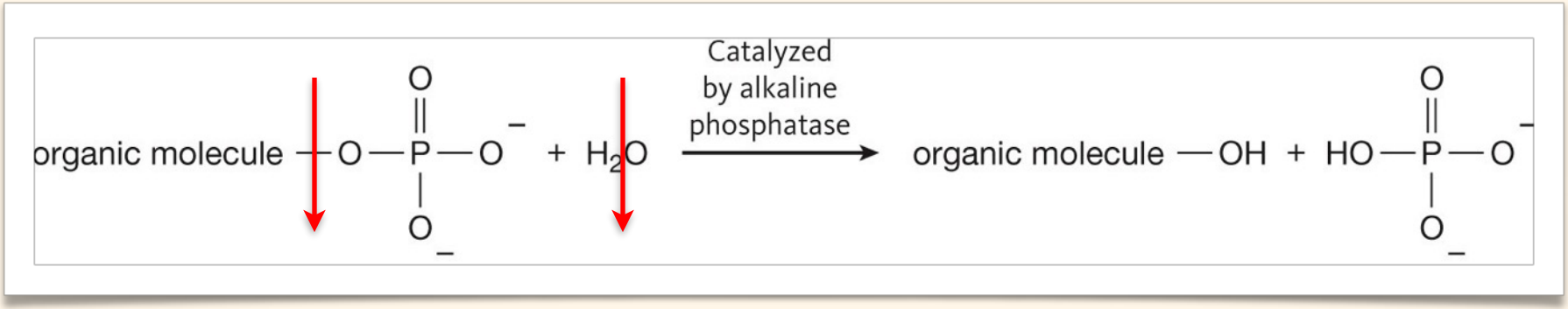

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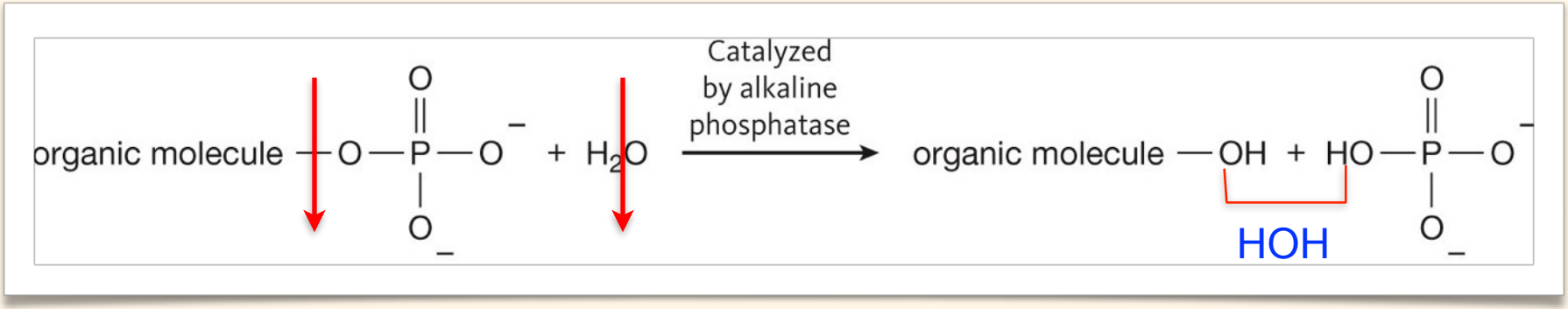

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- The reverse reaction is called **condensation**, and condensation reactions are used to make these large molecules from smaller ones.

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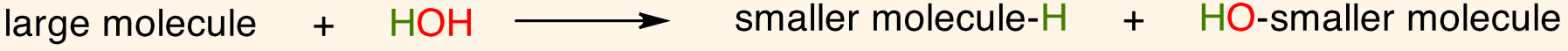

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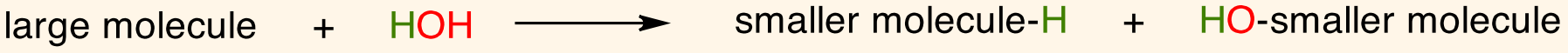

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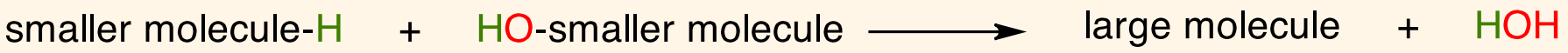
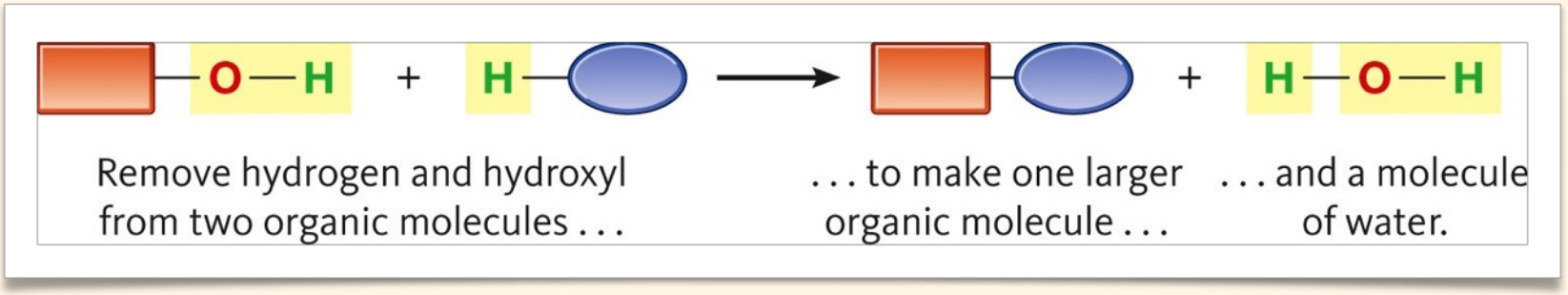


13.1 Introduction to Condensation Reactions: Ethers



Condensation versus Dehydration

- Unlike a dehydration reaction, in a **condensation** reaction, the H and OH come from different molecules.
- In a dehydration reaction, the H is removed from a carbon, but in a condensation reaction, the H is removed from an oxygen or a nitrogen.

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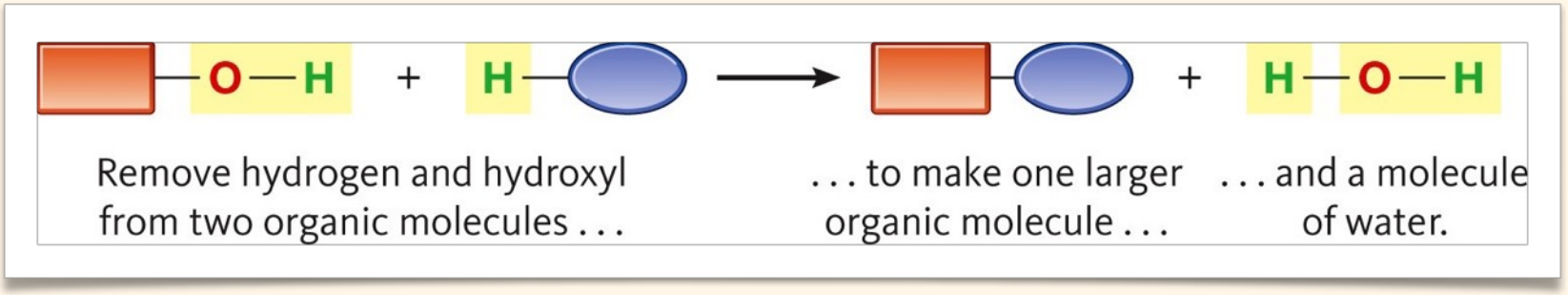

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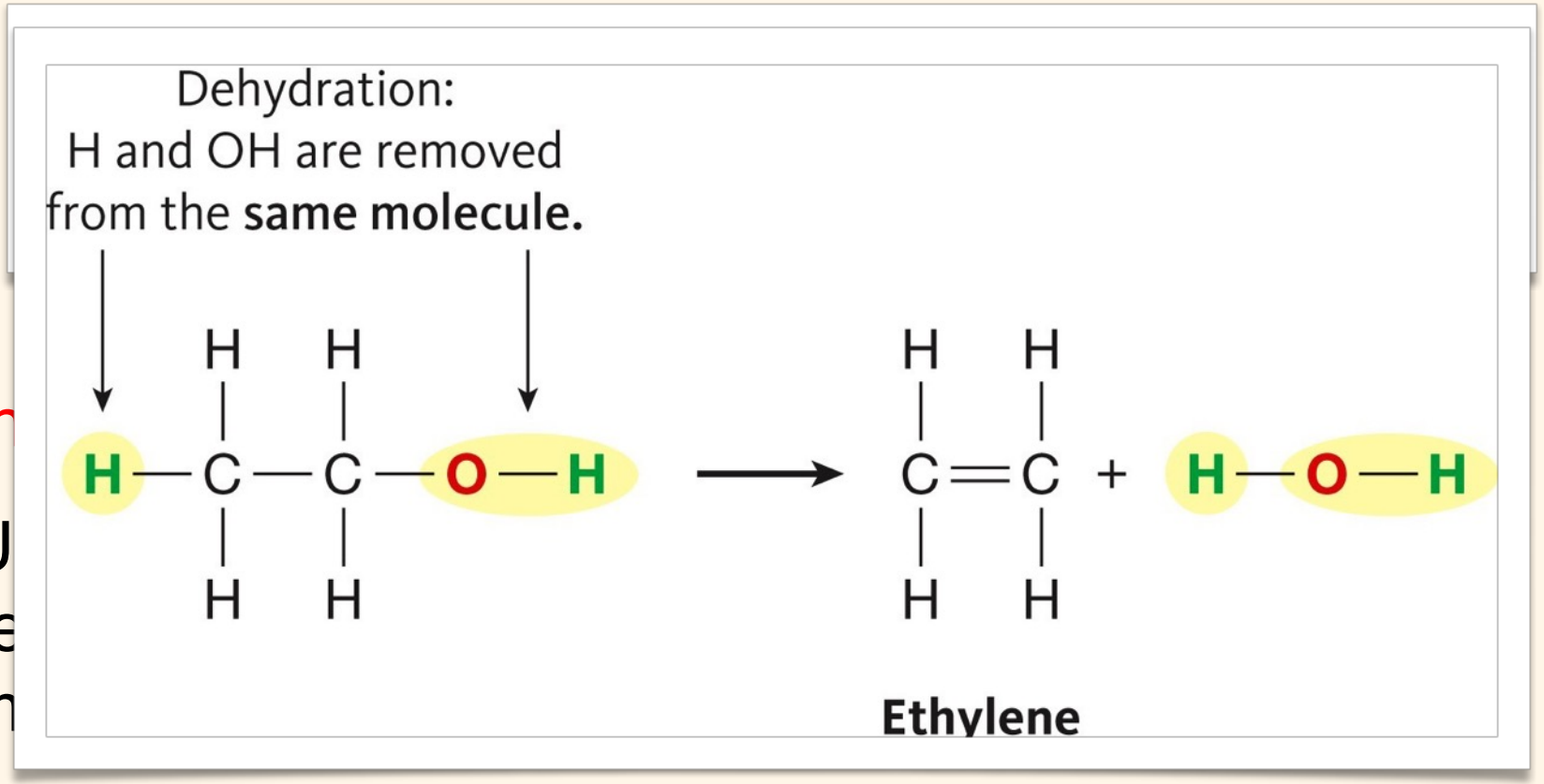

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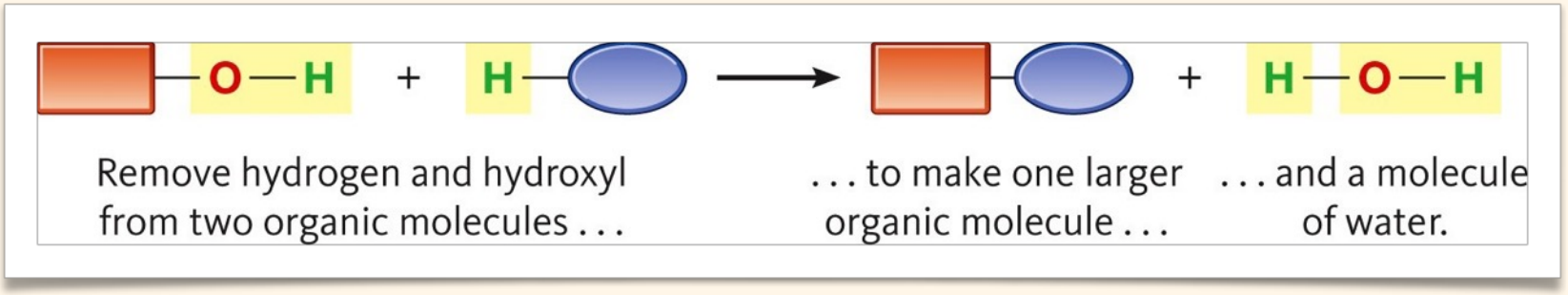

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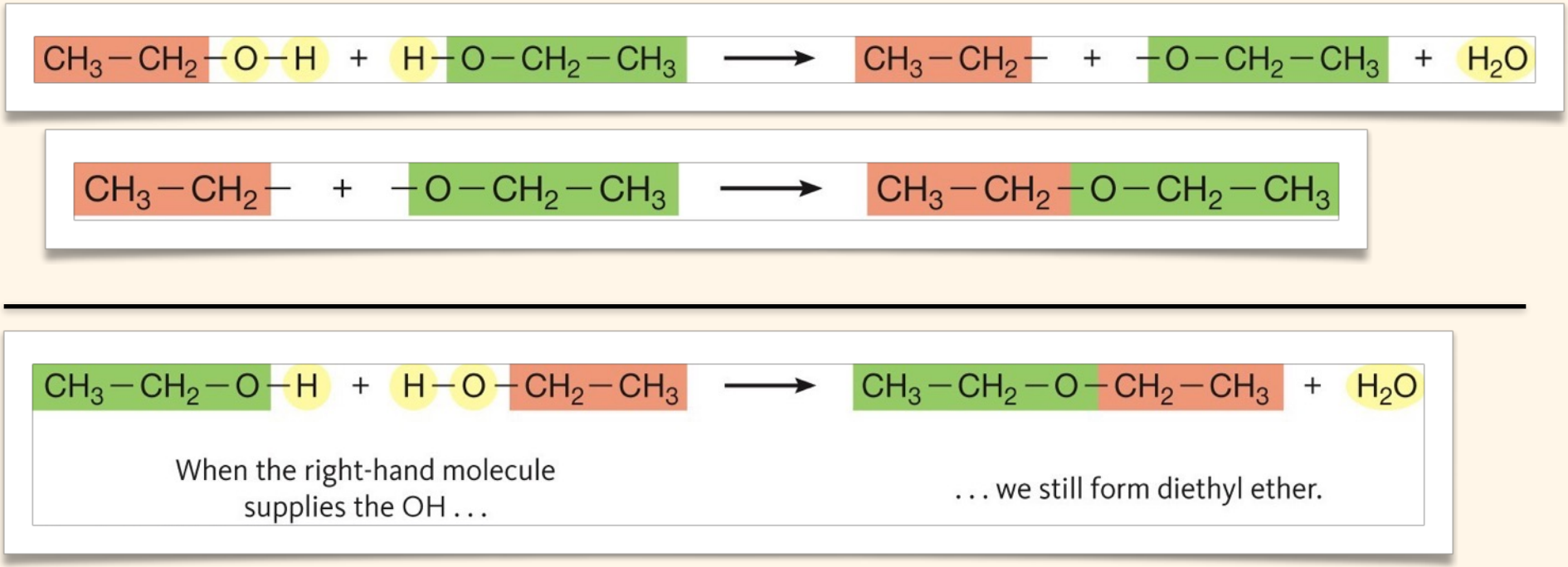
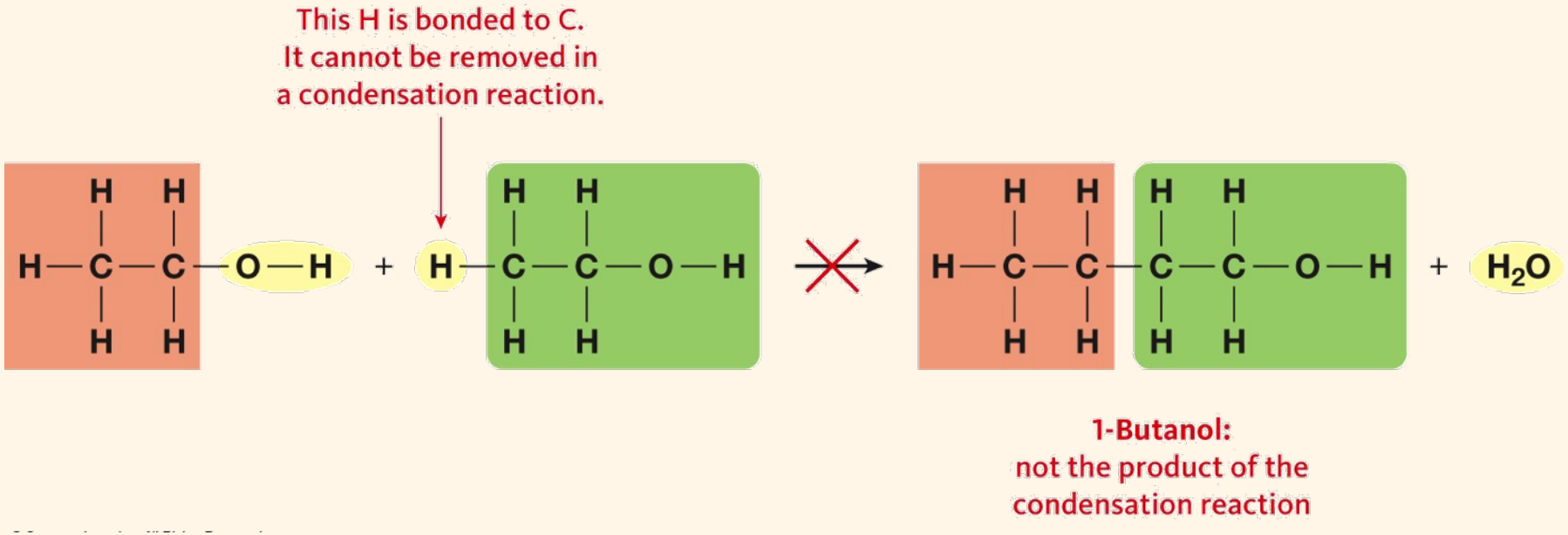
Formation of Ethers

- Example: Ethers are formed through a condensation reaction between two alcohols in which an H is removed from one alcohol and an OH is removed from another.



Be Aware of Which Hydrogen is Removed

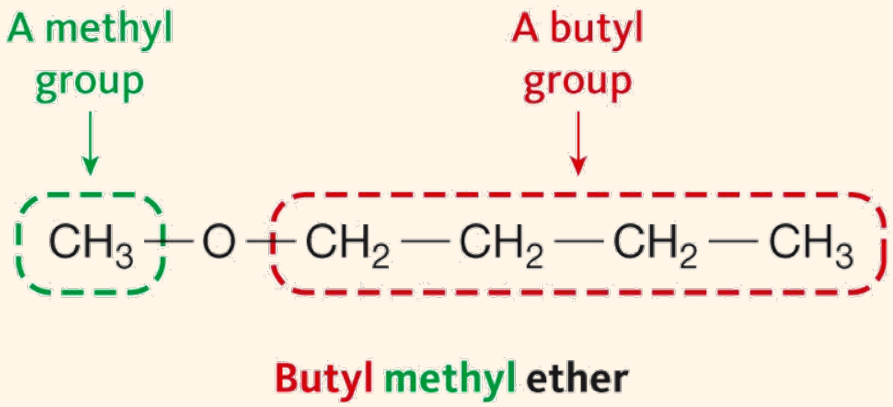
- Be sure that the H that you remove is removed from an OH or an NH in any condensation reaction.

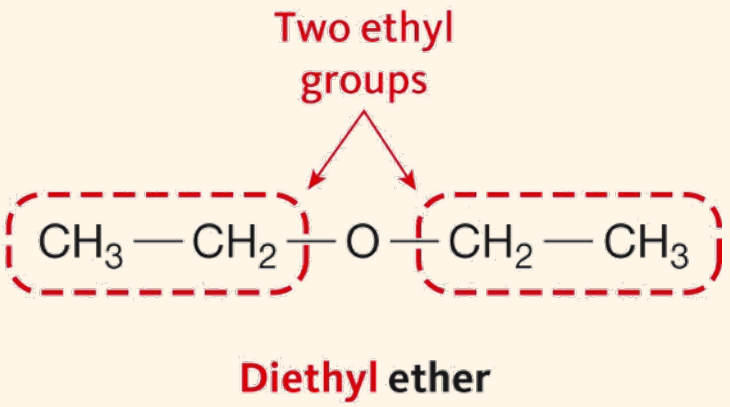


- It helps to draw the reactants structures such that the

Naming Ethers

- Ethers are commonly named by naming the alkyl group on either side of the ether, followed by the word *ether*
  - This is the same method we used for naming amines





Try It!

Question:

What is the name and structure of the product of a condensation reaction between methanol and 2-propanol??

13.2 Esterification, Amidation and Phosphorylation

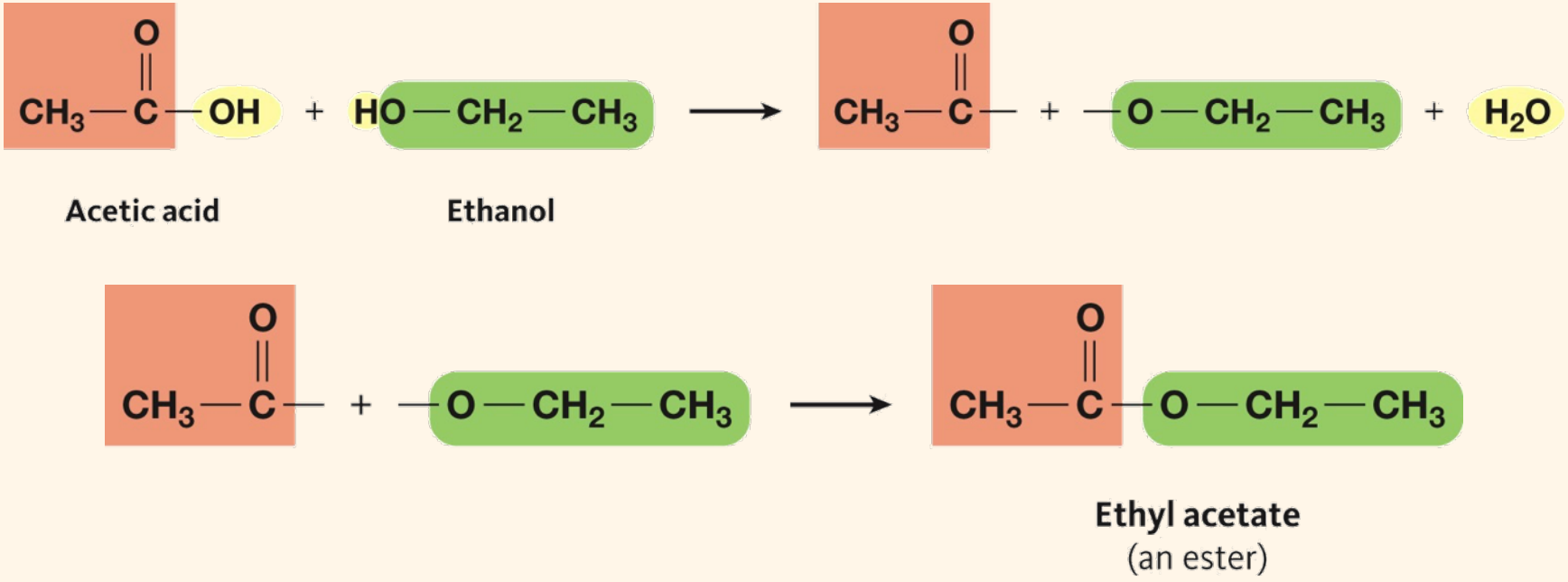
- Esterification, amidation and phosphorylation are all condensation reactions similar to the formation of ethers, only using different reactants.

TABLE 13.1 Four Common Condensation Reactions

Type of Reaction	Reactants	Products
Ether formation	Alcohol + alcohol	Ether + water
Esterification	Carboxylic acid + alcohol	Ester + water
Amidation	Carboxylic acid + amine	Amide + water
Phosphorylation	Phosphoric acid + alcohol	Phosphoester + water

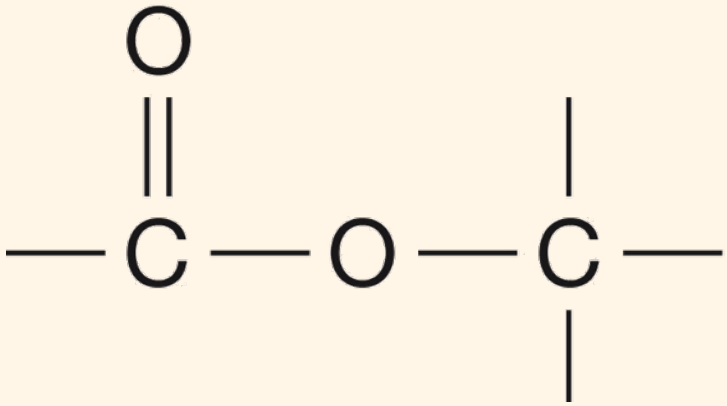
Esterification

- A **carboxylic acid** reacts with an **alcohol** to form an **ester** in esterification reactions.
- The carboxylic acid loses the OH and the alcohol loses the H to form an ester and the water by-product.



Esters

- The ester functional group is similar to a carboxylic acid, except that the O is not bonded to an H.

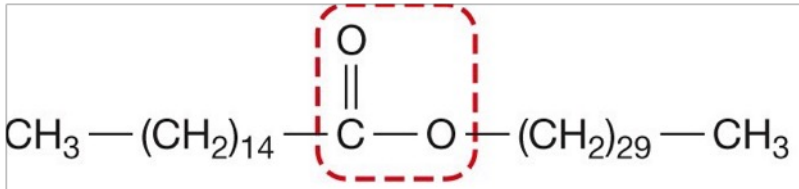


The ester functional group

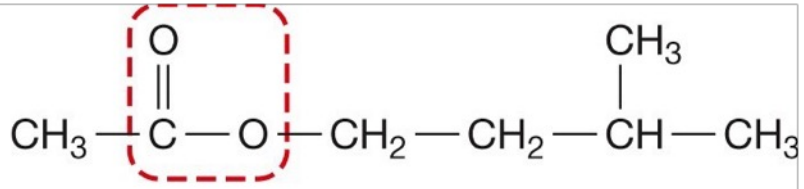
- Esters are very stable and don't react easily
- Examples of esters include some fats and oils and waxes. Esters are responsible for characteristic flavors and odors of many fruits.

Esters

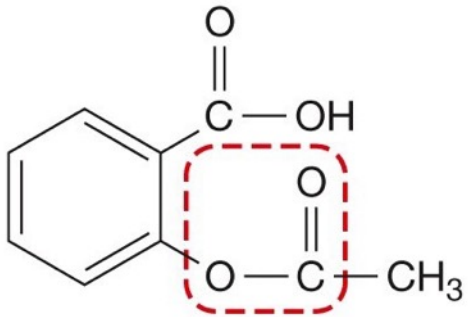
- Unlike carboxylic acids, esters often have pleasant odors.



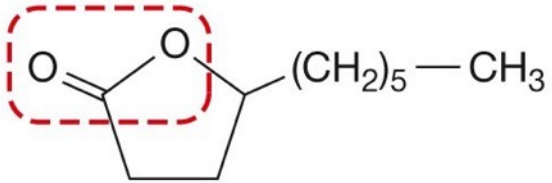
Myricyl palmitate
(a component of beeswax)



Isoamyl acetate
(banana flavor)



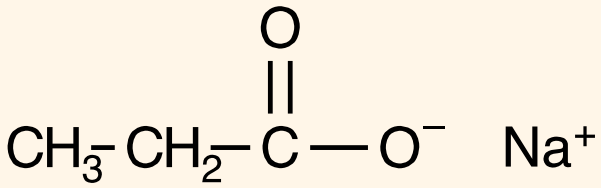
Aspirin

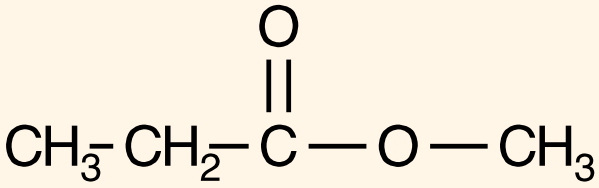


Gamma-decalactone
(peach flavor)

Esters

- Esters are named similarly to the conjugate bases of carboxylic acids





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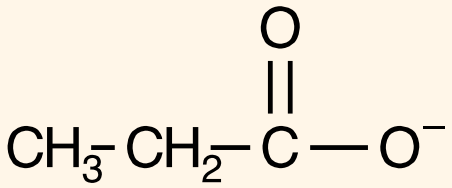
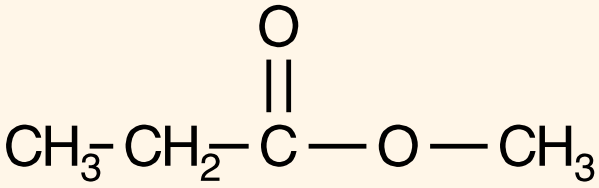


Na^+

sodium propanoate



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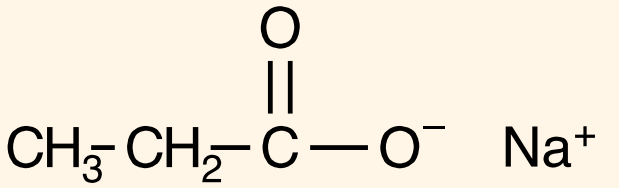
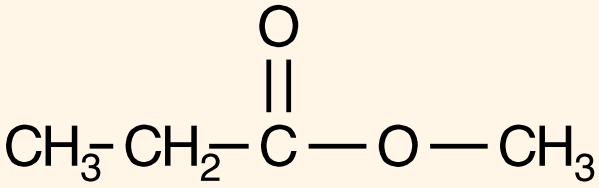


Na^+

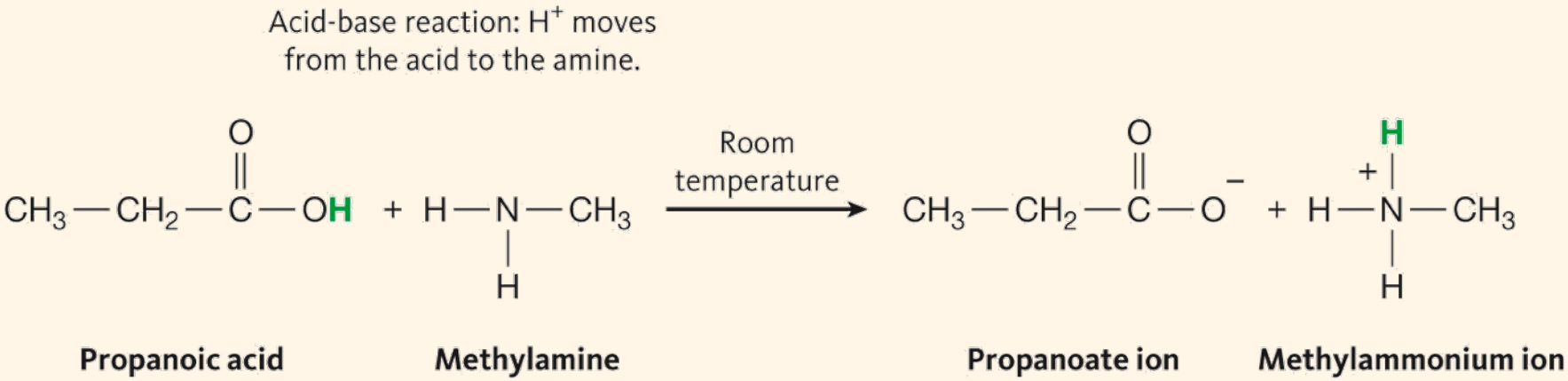
sodium propanoate



methyl propanoate

Amidation Reaction Conditions

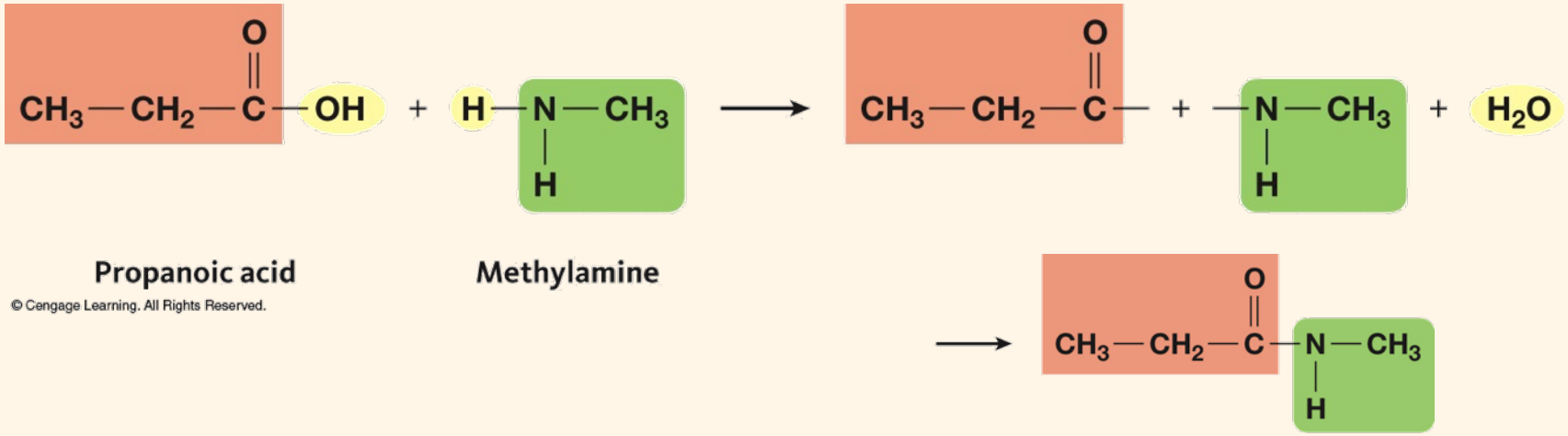
- At room temperature, combining a carboxylic acid and an amine results in an acid-base reaction.



- For an **amidation** reaction to occur, the reaction must be heated above 100 °C

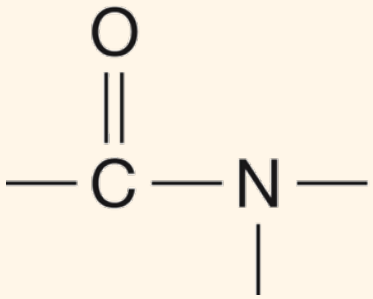
Amidation

- A carboxylic acid reacts with an amine (primary, secondary or ammonia) to form an amide in amidation reactions.
- The carboxylic acid loses the OH and the amine loses the H to form the amide and the water by-product.



Amides

- An amide functional group is a carbonyl bonded to a nitrogen (which may have two H, two alkyl groups or one H and one alkyl group attached)

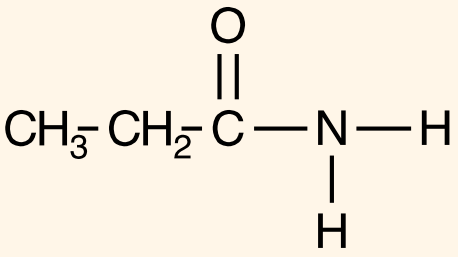


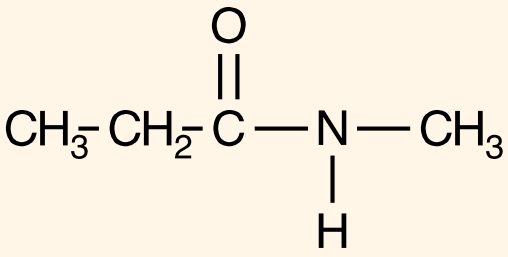
The **amide** functional group

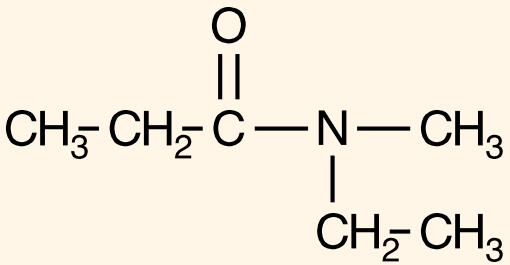
- Unlike amines, amides are not basic
- Proteins, acetaminophen (Tylenol), and saccharine all contain amide functional group(s).

Amides

- The IUPAC ending for amides is -*amide*.
- If there are alkyl groups attached to the amide nitrogen, their locations are indicated by using the letter "*N*"







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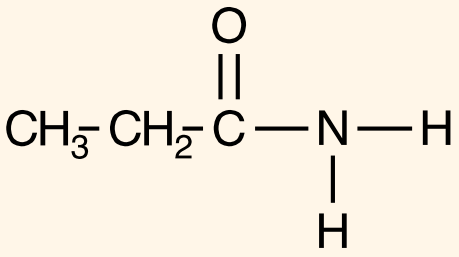
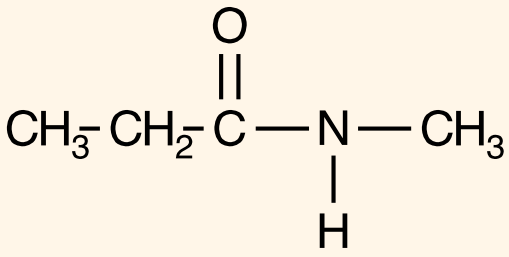
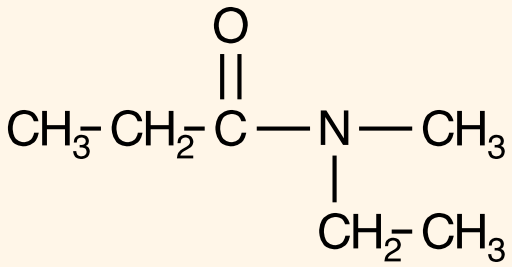


propanamide





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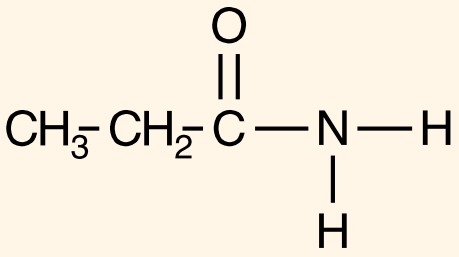
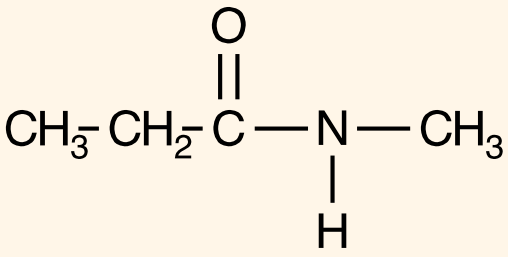
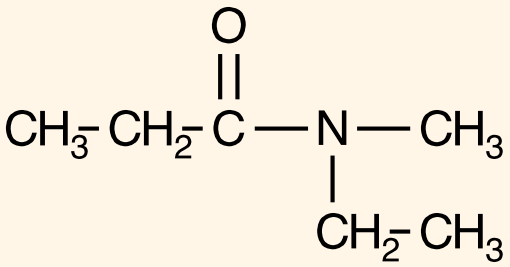


propanamide



N-methylpropanamide



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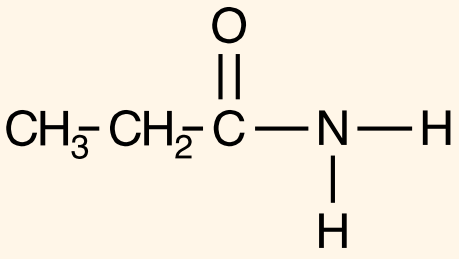
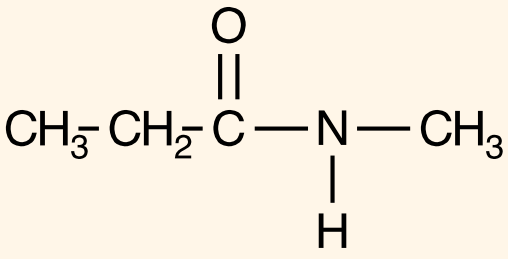
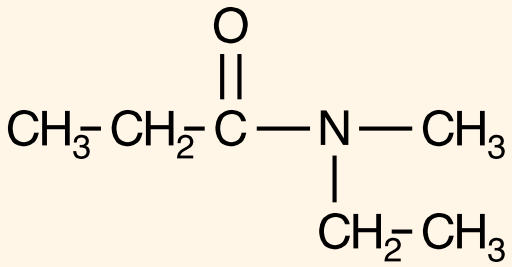


propanamide



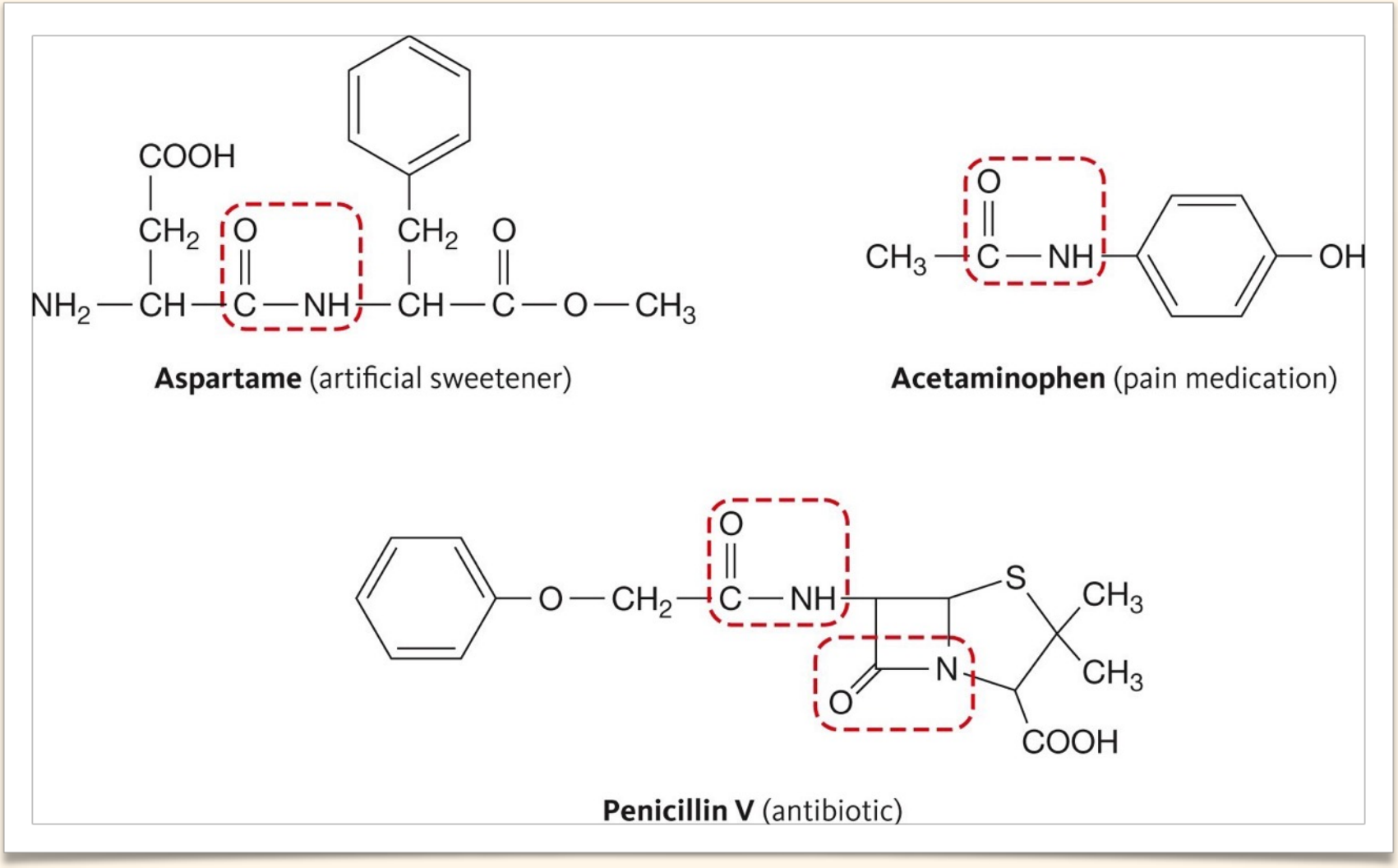
N-methylpropanamide



N-ethyl-*N*-methylpropanamide

Amides

- Some common amides



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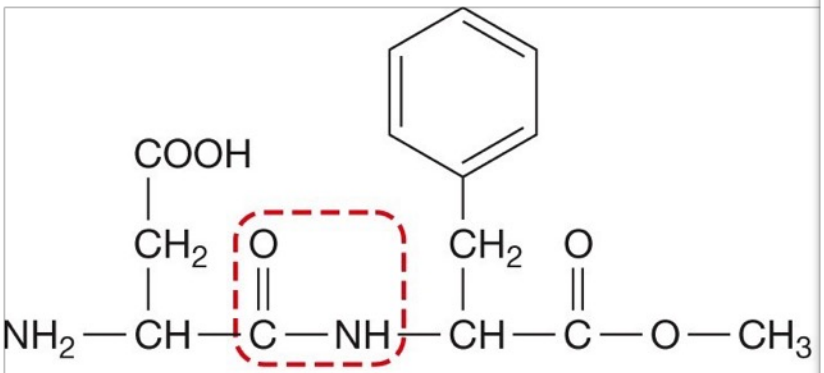
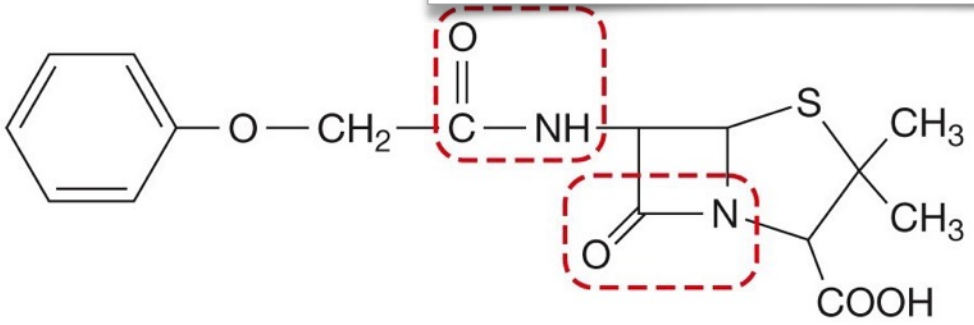


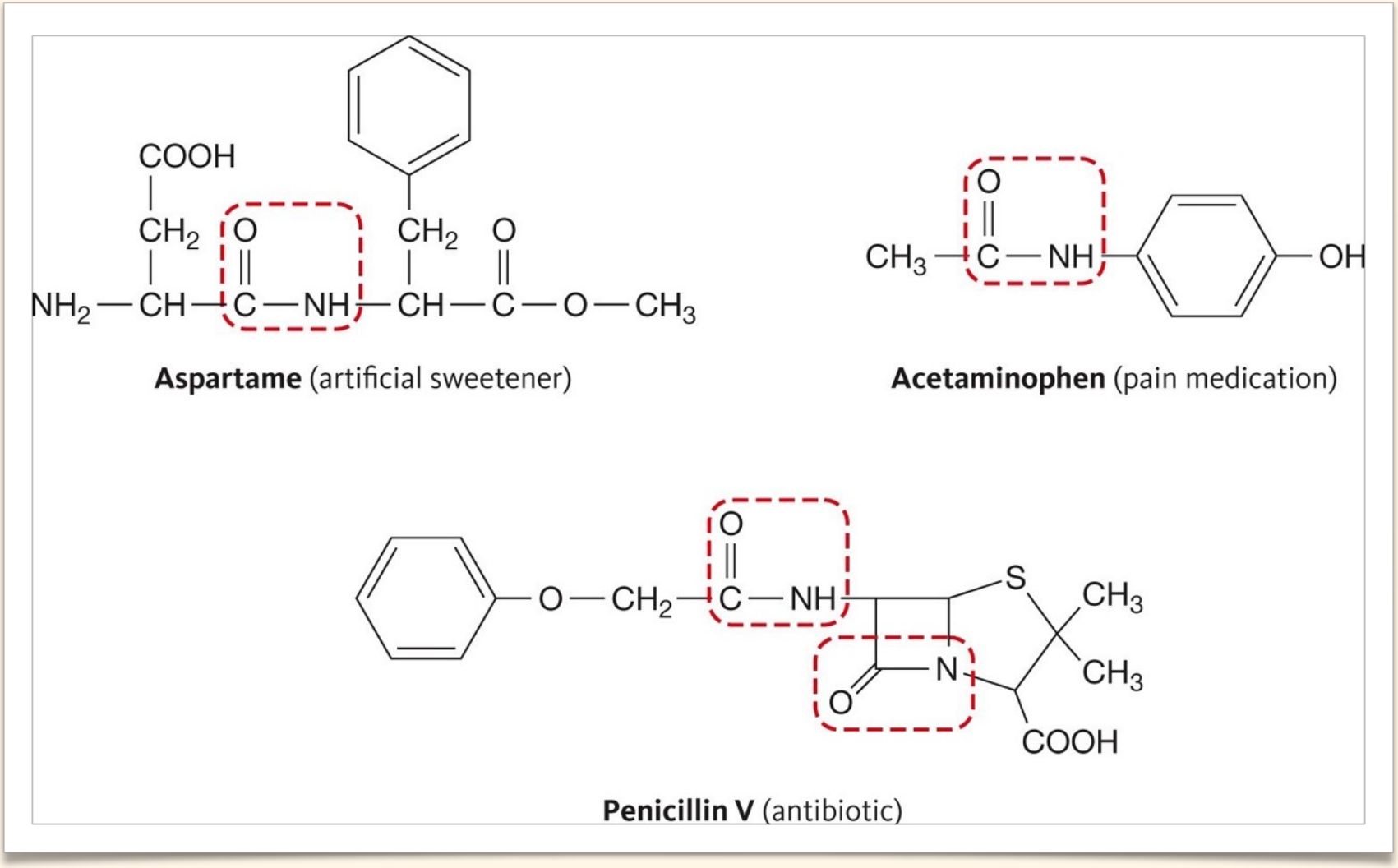
Aspartame (artificial sweetener)



Penicillin V (antibiotic)

Amides

- Some common amides



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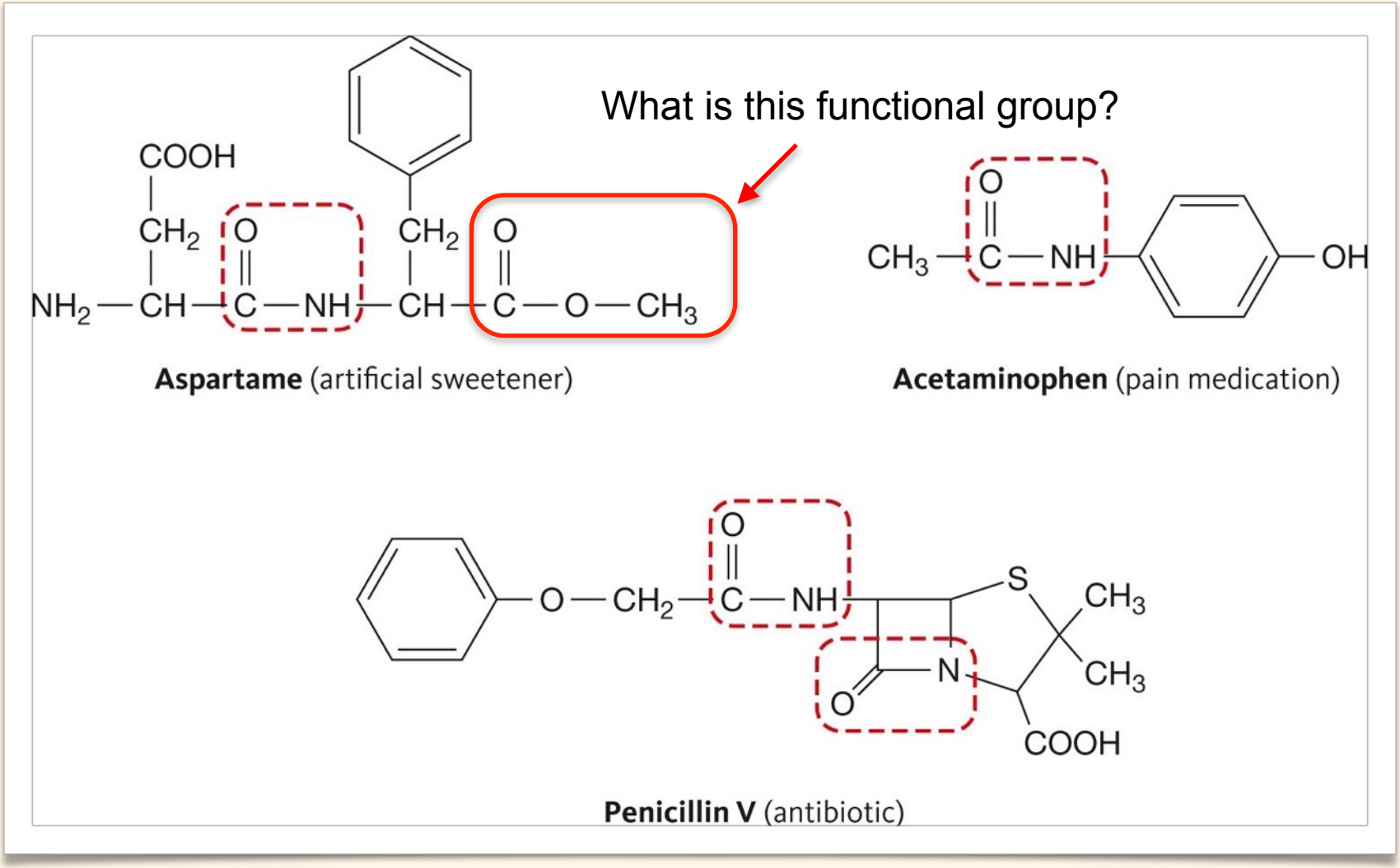

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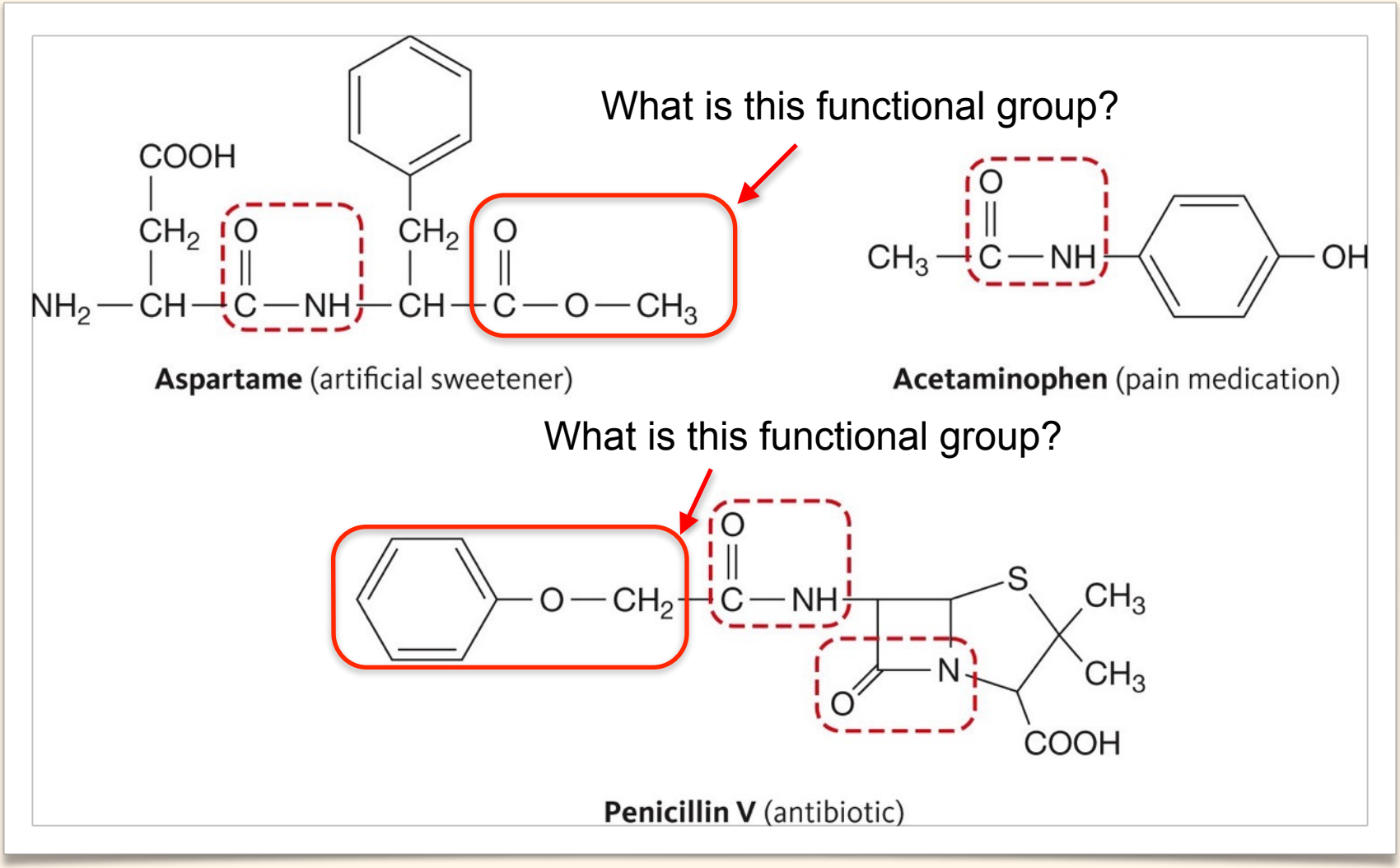
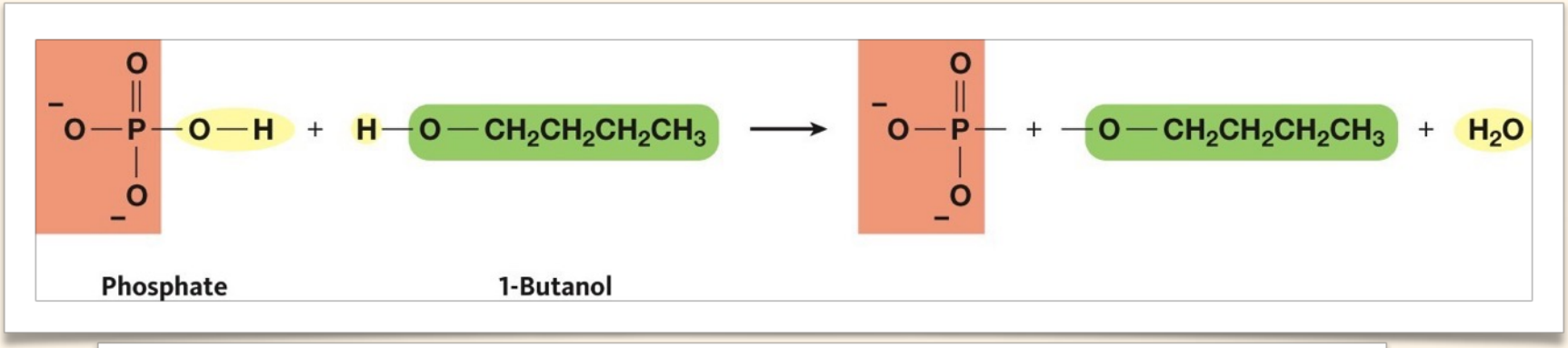
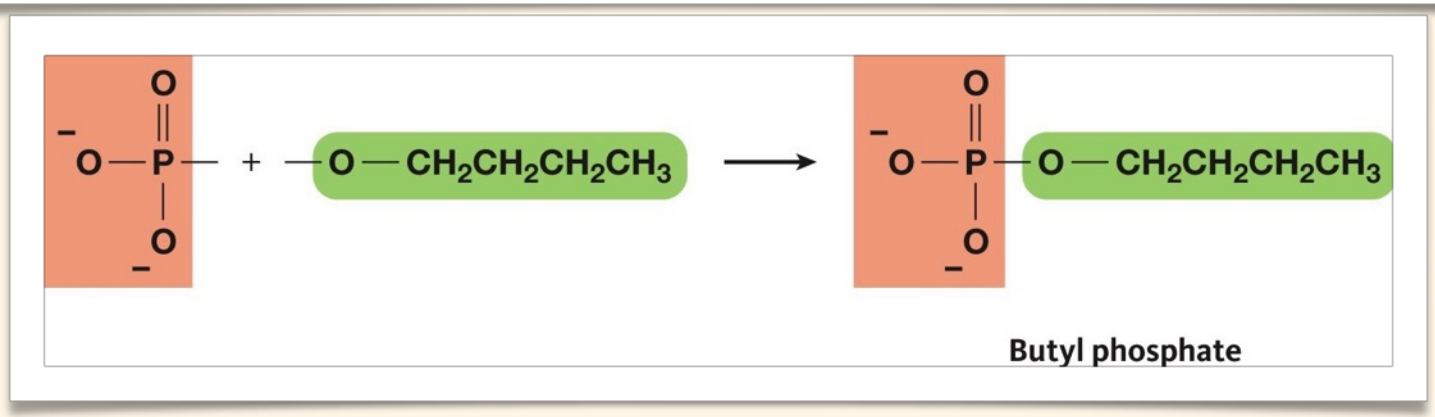


Phosphorylation Reactions

- A alcohol reacts with a phosphate group on an organic molecule to form a phosphoester in a phosphorylation reaction.
- The phosphate group loses the OH and the alcohol loses the H to form a phosphoester and the water by-product.





Phosphorylation Reactions

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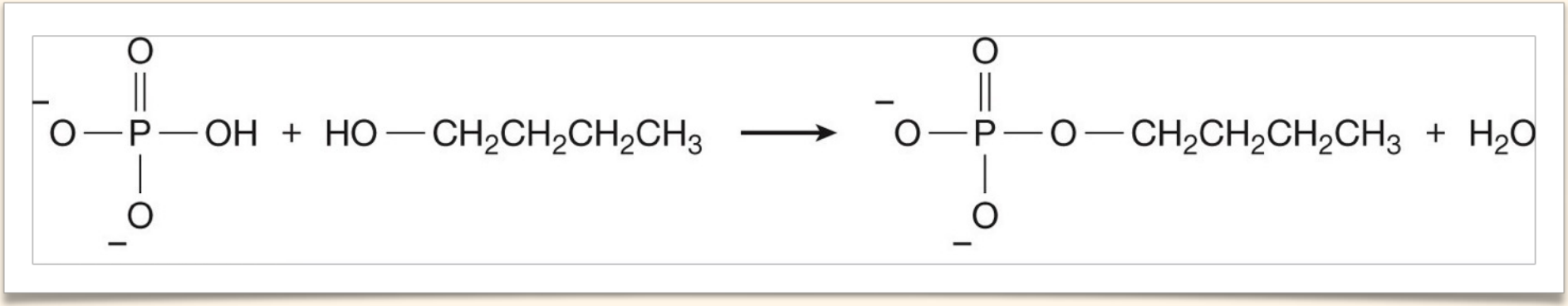
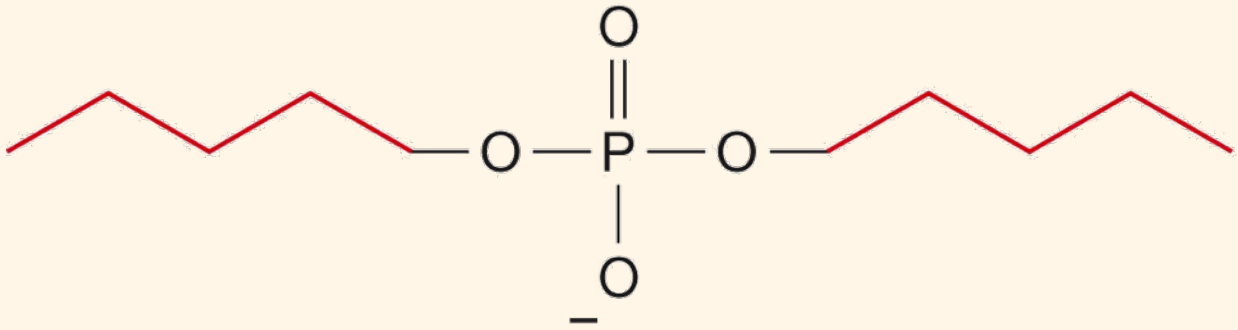


Phosphoesters and Phosphodiesters

- Phosphoesters are common biochemical molecules used for energy.
- Phosphates can make two esters
  - Phosphodiesters are found in DNA, RNA, NAD^+, FAD and phospholipids.



The general structure of a phosphodiester

Try It!

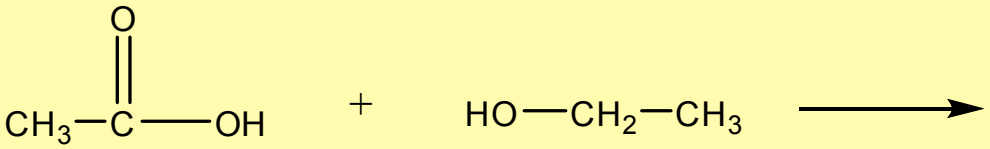
Question:

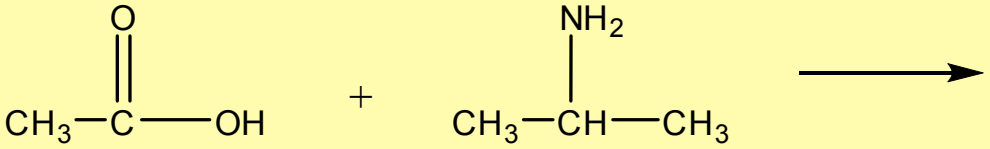
Complete the following reaction equations and name the organic product.

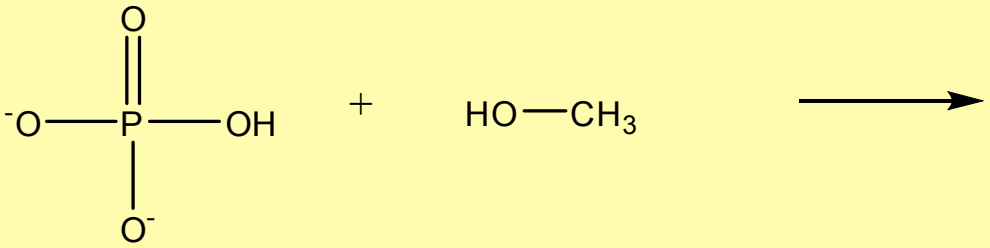
Try It!

Question:

Complete the following reaction equations and name the organic product.



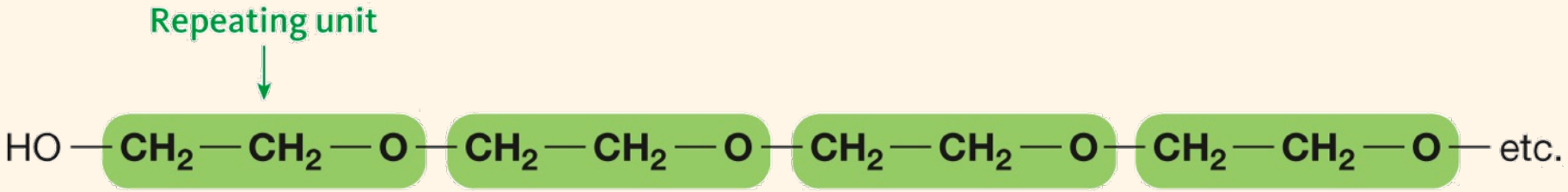




13.3 Condensation Polymers

- Molecules which contain more than one O-H or N-H group (or one of each) can react to form a longer chain polymer (a large molecule made by linking many small units).
- Ethylene glycol contains two hydroxyl groups and can form a polymer with repeating units.

Diethylene glycol



Polyethylene glycol

13.3 Condensation Polymers

- Mole
  one
  mole
- Ethy
  poly

p (or
large

m a

HO — CH

+ H_2O

HO — C

O — etc.

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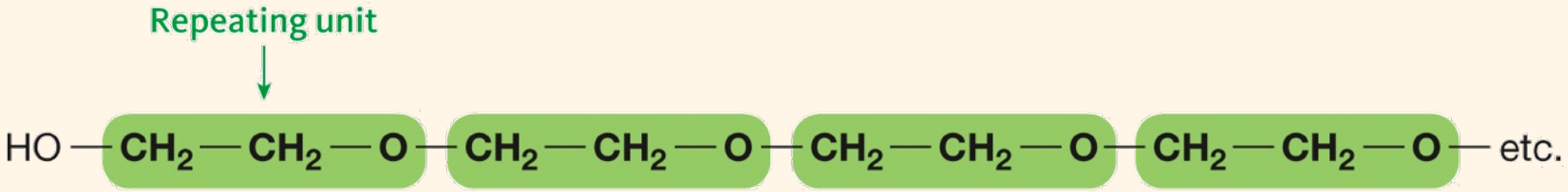
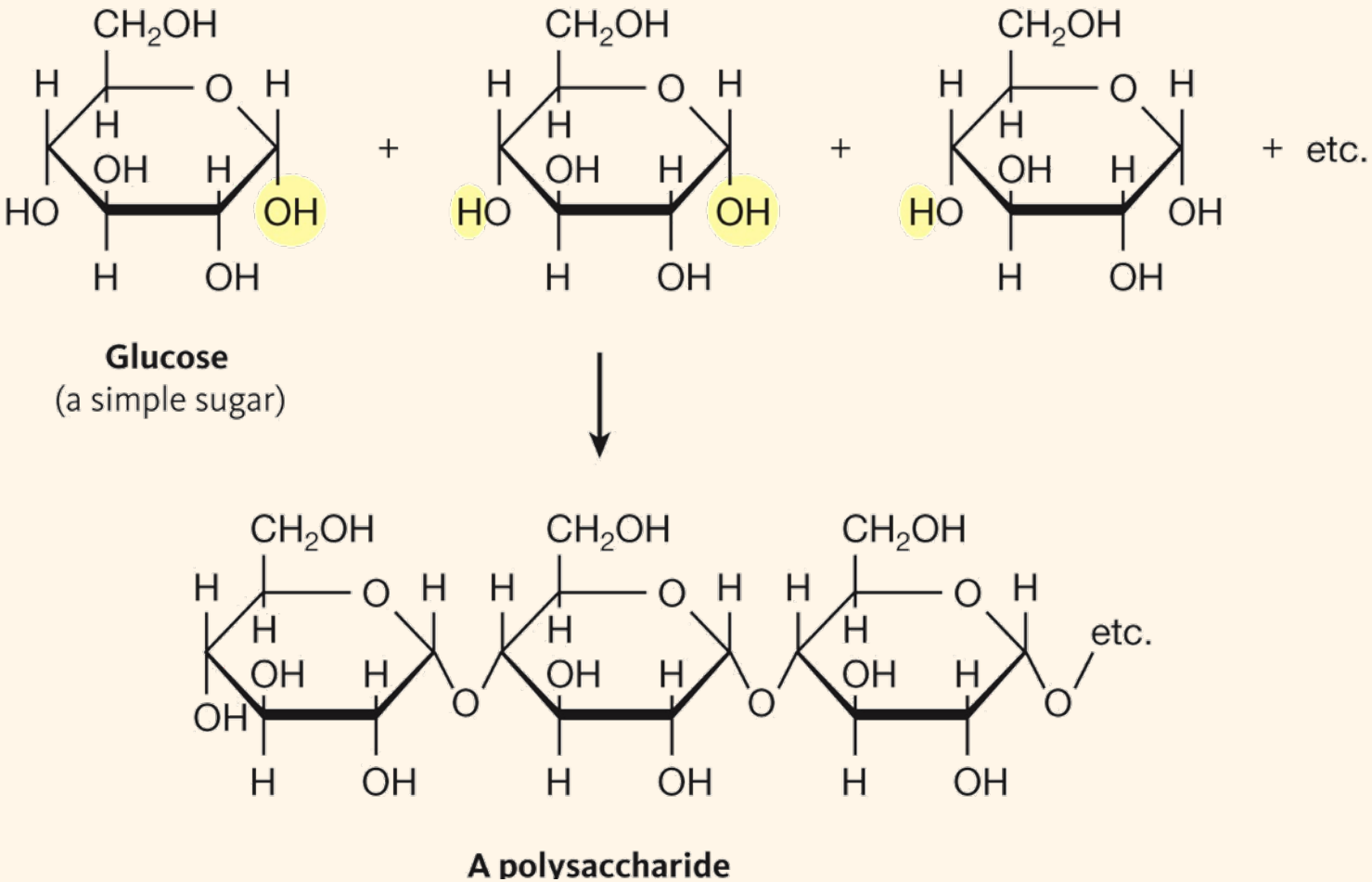


Polyethylene glycol

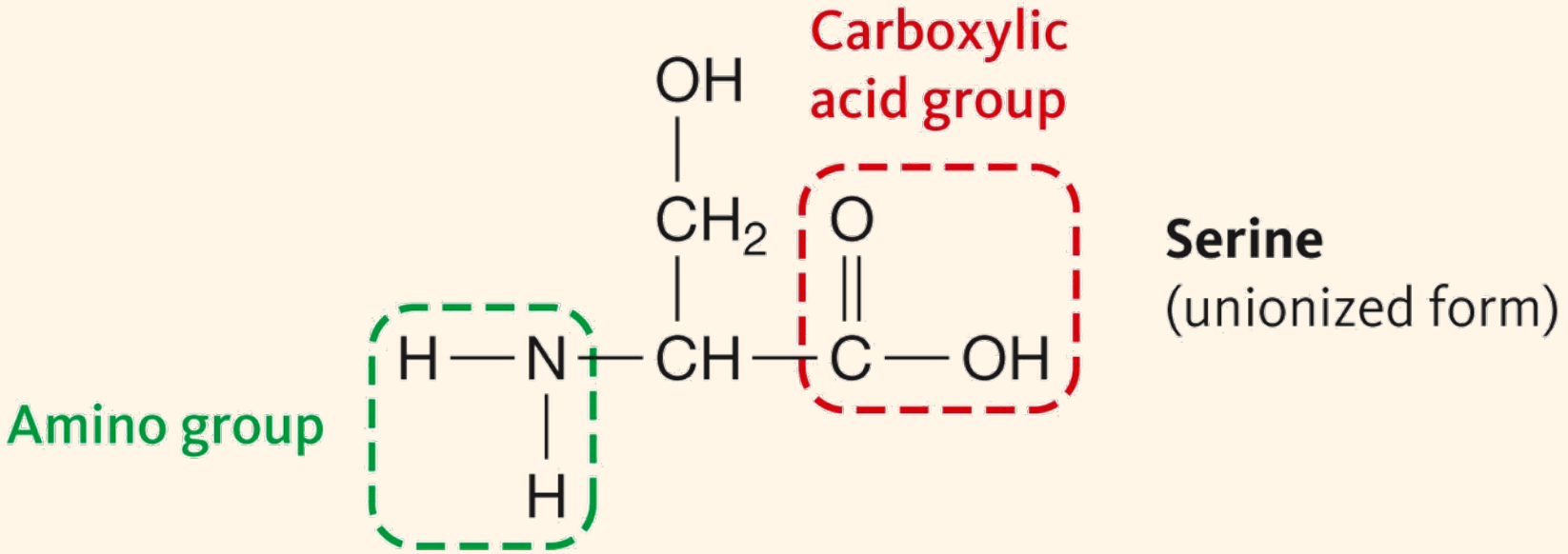
Polysaccharides

- Simple sugars condense to form more complex carbohydrates



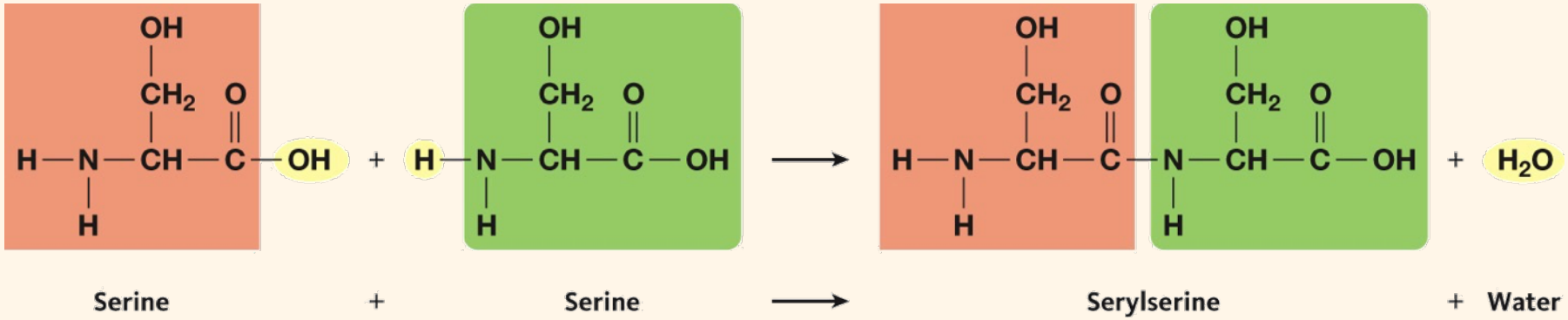
Amino Acids and Proteins

- Amino acids are the smaller units that make up larger proteins.
- Amino acids contain both a carboxylic acid group and an amino group and thus are well suited to form polymers.



Amino Acids and Condensation

- The carboxylic acid group of one amino acid can condense with the amine group of another amino acid.

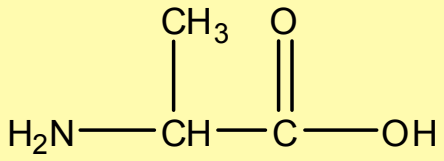


- Proteins long chains made by condensing many different amino acids.

Try It!

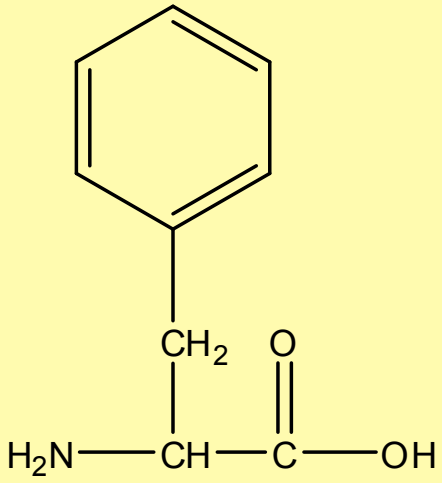
Question:

Connect the following three amino acids using condensation reactions.



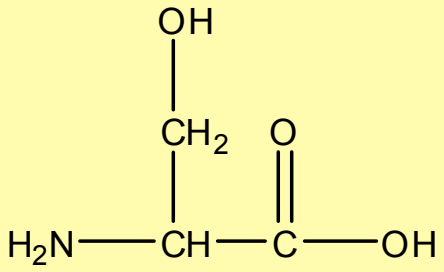
Alanine

ALA



Phenylalanine

PHE

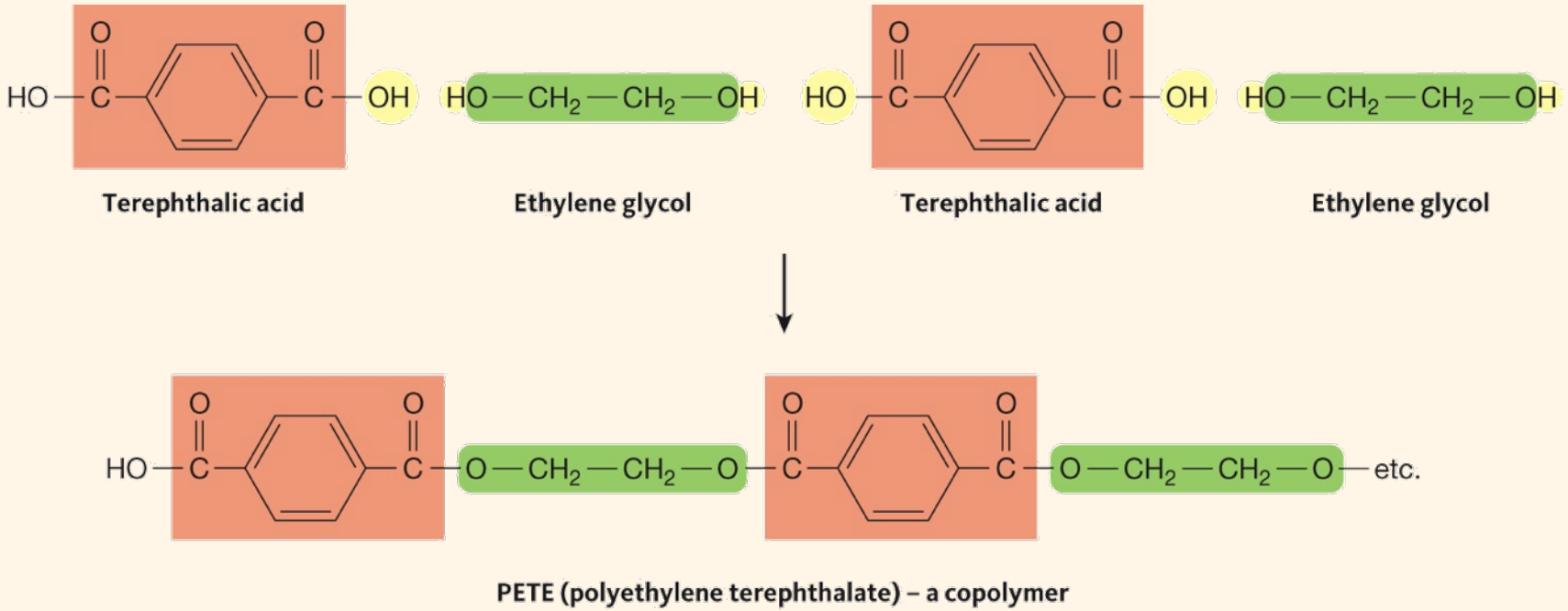


Serine

SER

Condensation Polymers

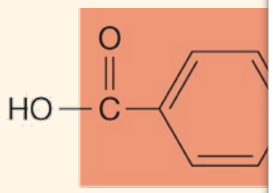
- Condensation Polymers are important in many common materials
- PETE (polyethylene terephthalate) is an example of a copolymer because it is made from two different starting materials.



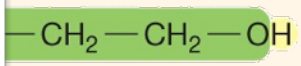
PETE (polyethylene terephthalate) – a copolymer

Condensation Polymers

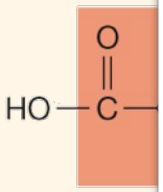
- Condens any common
- PETE (p ample of a copoly ifferent starting

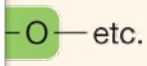


Terephthalic



Ethylene glycol





Condensation Polymers

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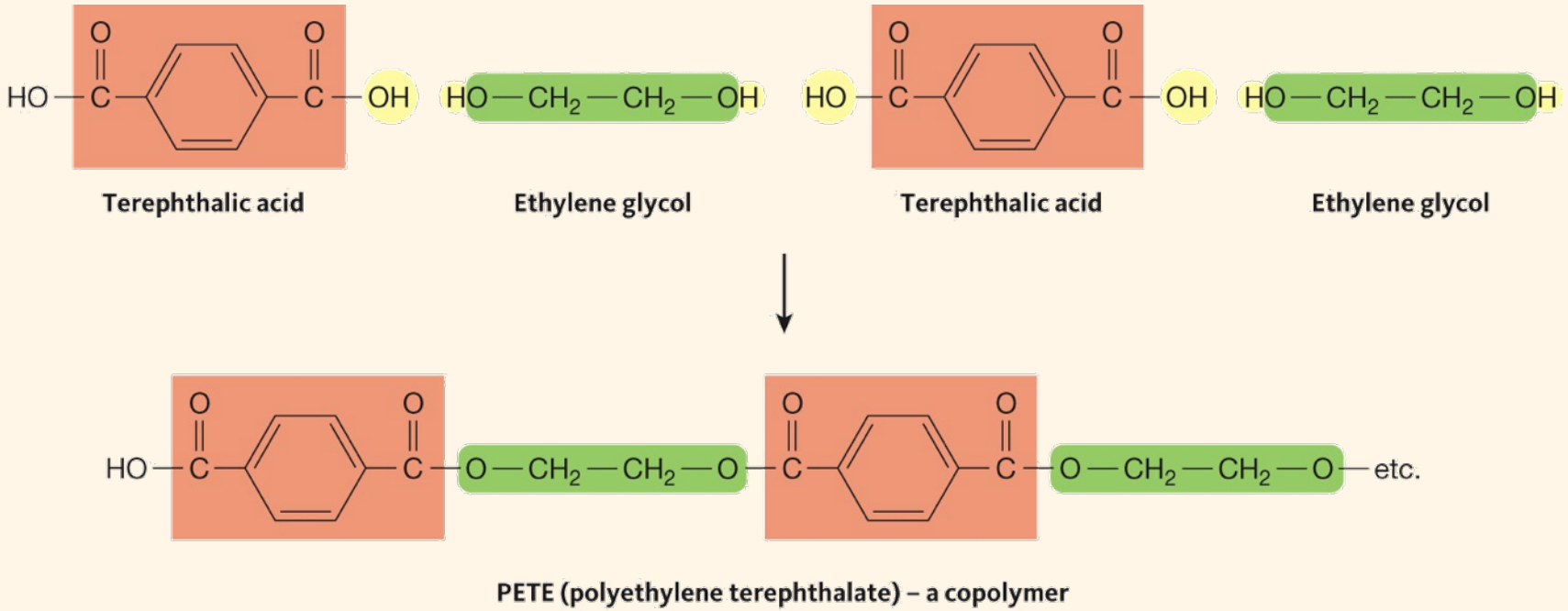
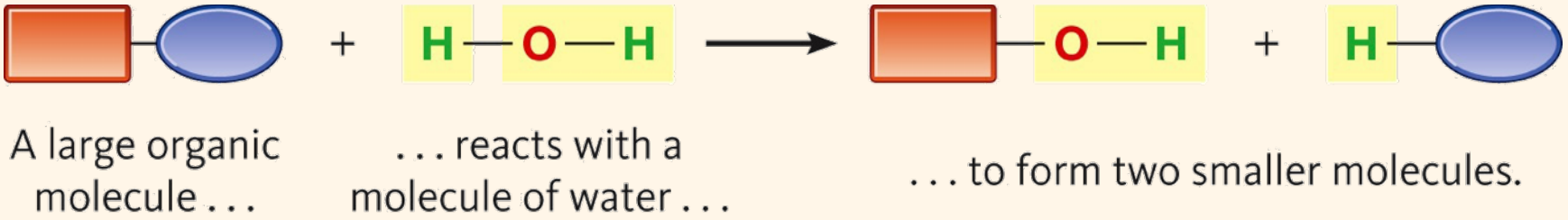
- PETE (polyethylene terephthalate) is an example of a copolymer because it is made from two different starting materials.



PETE (polyethylene terephthalate) – a copolymer

13.4 Hydrolysis

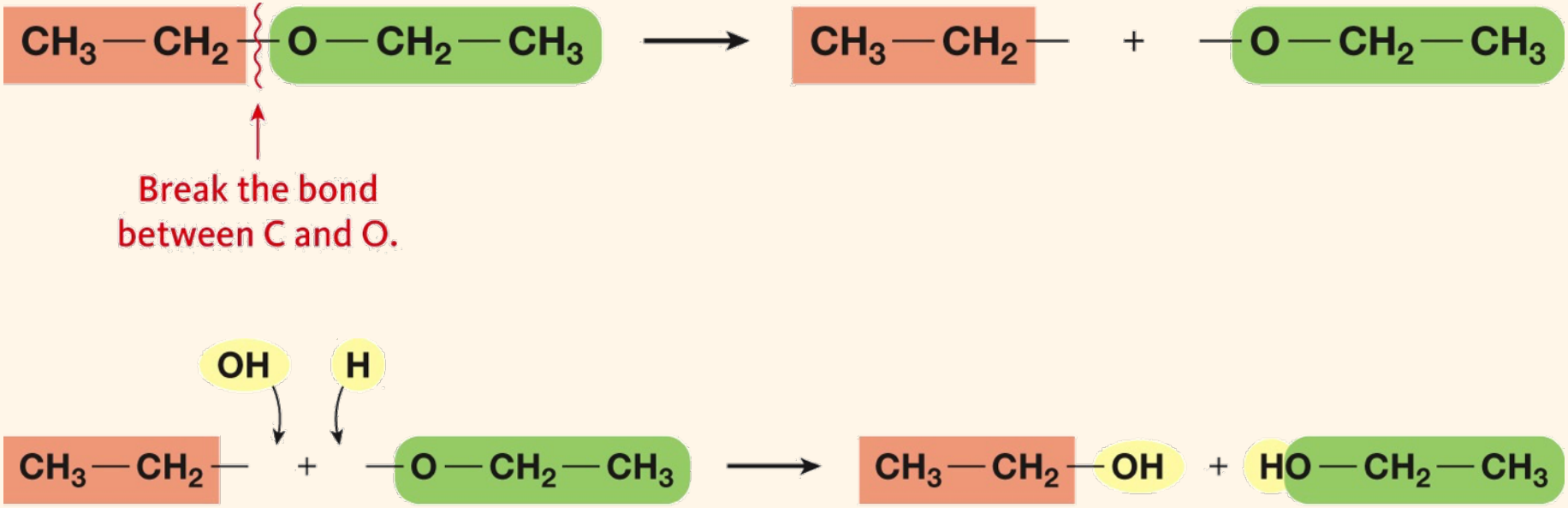
- Hydrolysis is the opposite of condensation: a large molecule reacts with water to produce two smaller molecules



- In this section, we will look at the hydrolysis of ethers, esters and amides.

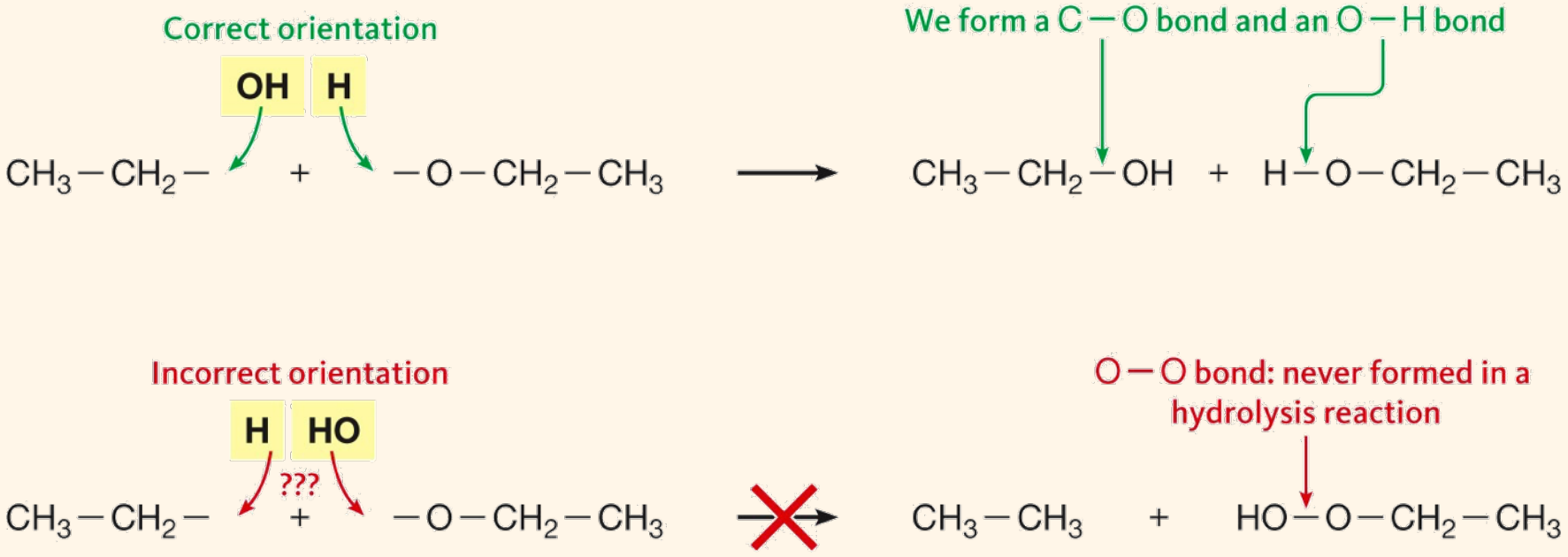
Ether Hydrolysis

- In ether hydrolysis, one of the bonds between C and O breaks, and H and OH from water are added to each fragment.



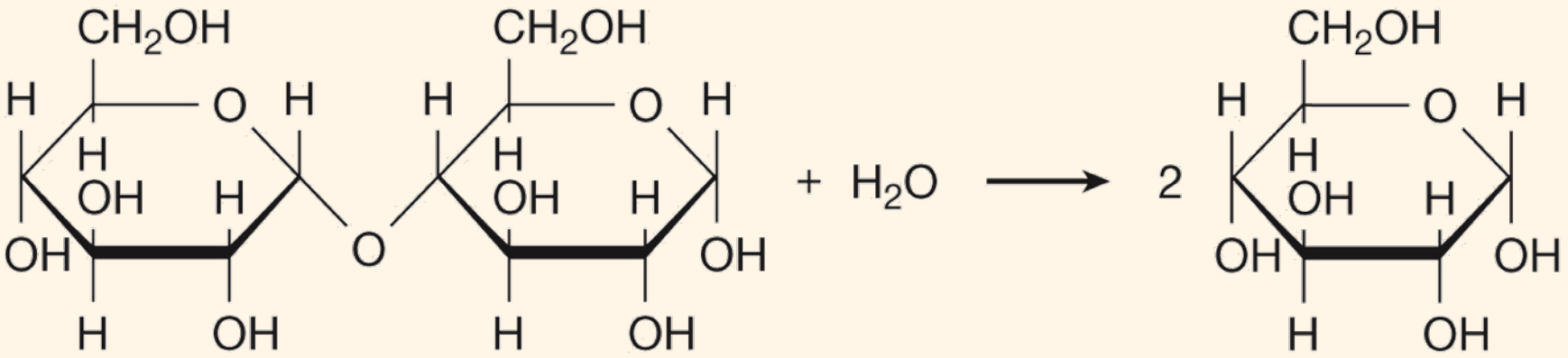
Where to add the H and OH

- Be careful about placing the H and the OH. The fragment which contains the oxygen should add the H and never the OH.



Example: The Hydrolysis of Maltose

- Maltose, a disaccharide containing two glucose molecules, is hydrolyzed by cells to obtain two glucose molecules, a simple sugar used directly for energy.

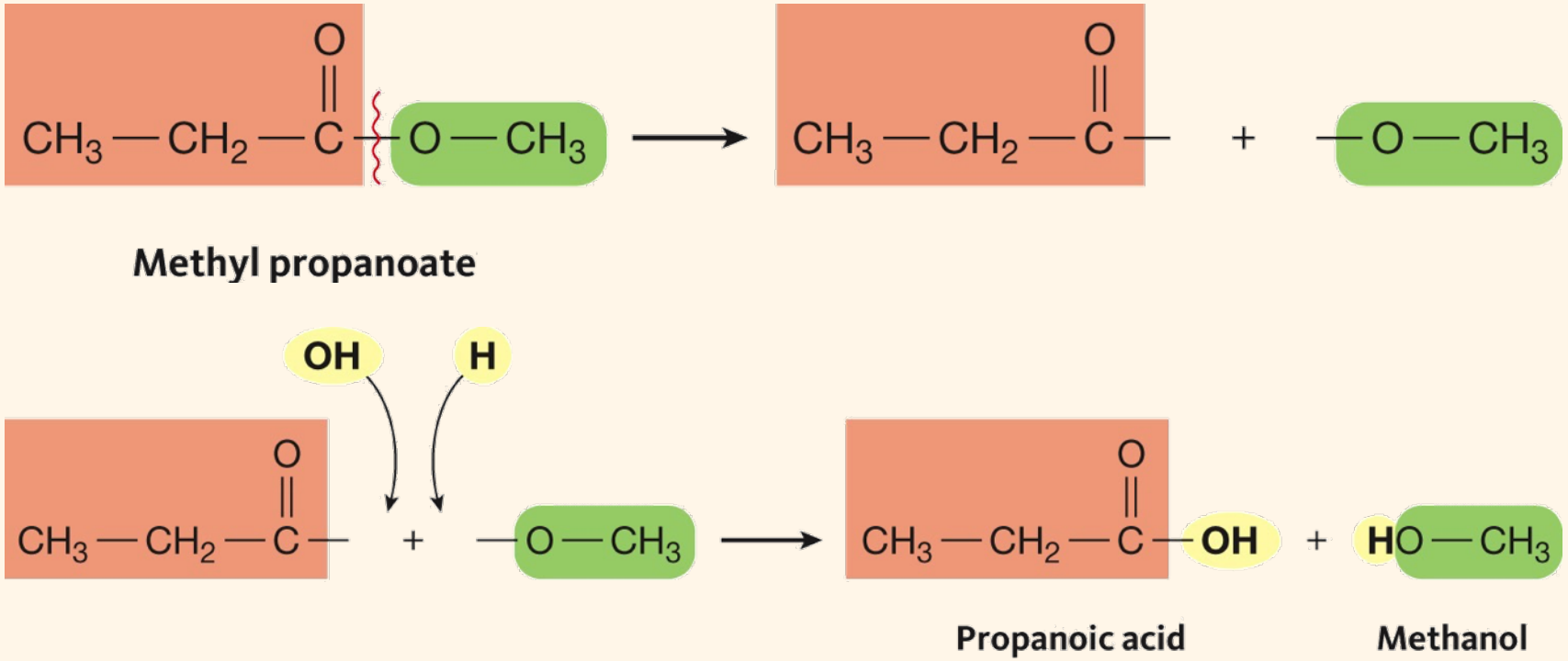


Maltose –
a disaccharide

Glucose –
a simple sugar

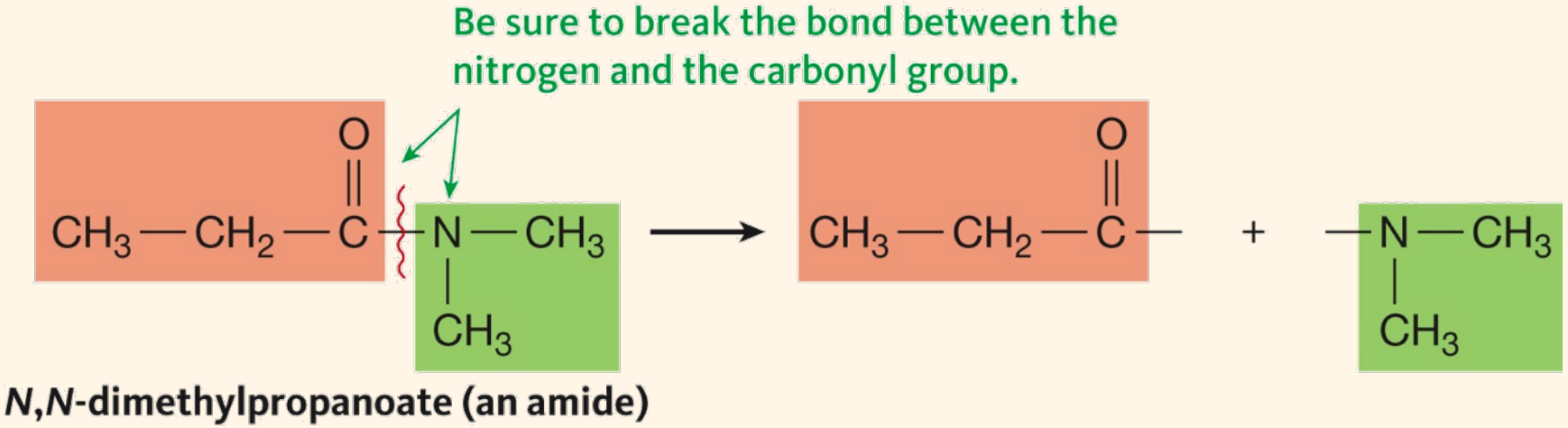
Hydrolysis of Esters

- In ester hydrolysis, the C-O bond is broken, and H and OH from water are added to the fragments.
- The H is added to the fragment containing the O a (producing an alcohol) and the OH is added to the fragment containing the carbonyl (producing a carboxylic acid).



Hydrolysis of Amides

- In amide hydrolysis, the C-N bond is broken, and H and OH from water are added to the fragments.
- The H is added to the fragment containing the N a (producing an amine) and the OH is added to the fragment containing the carbonyl (producing a carboxylic acid).



N,*N*-dimethylpropanoate (an amide)

Hydrolysis of Amides

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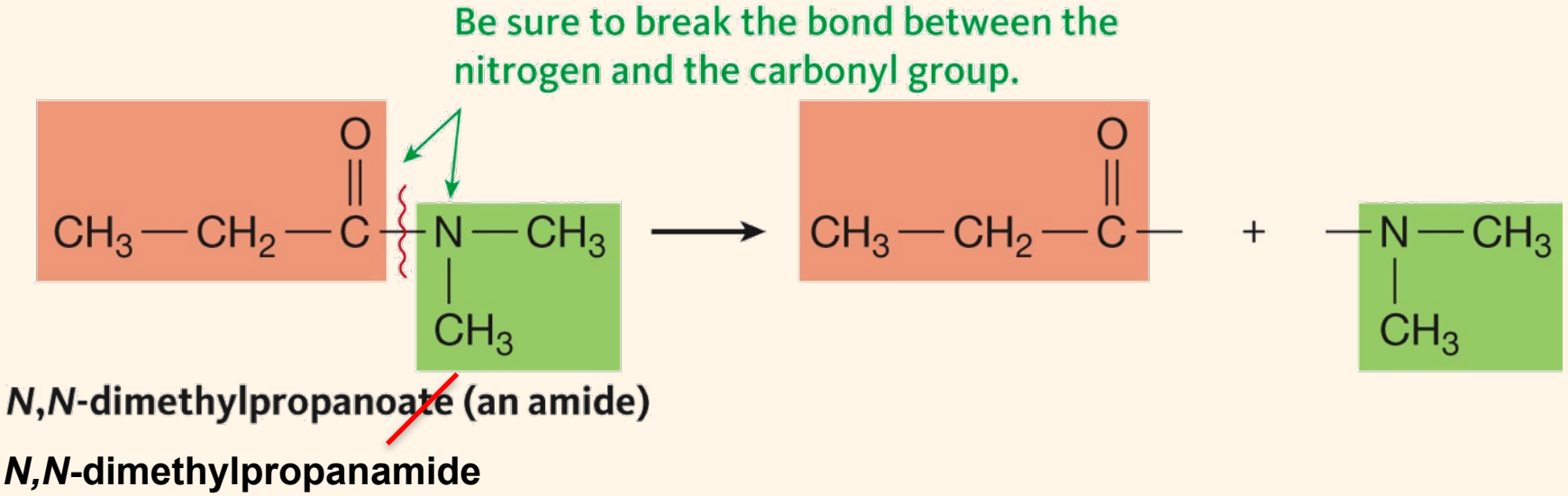
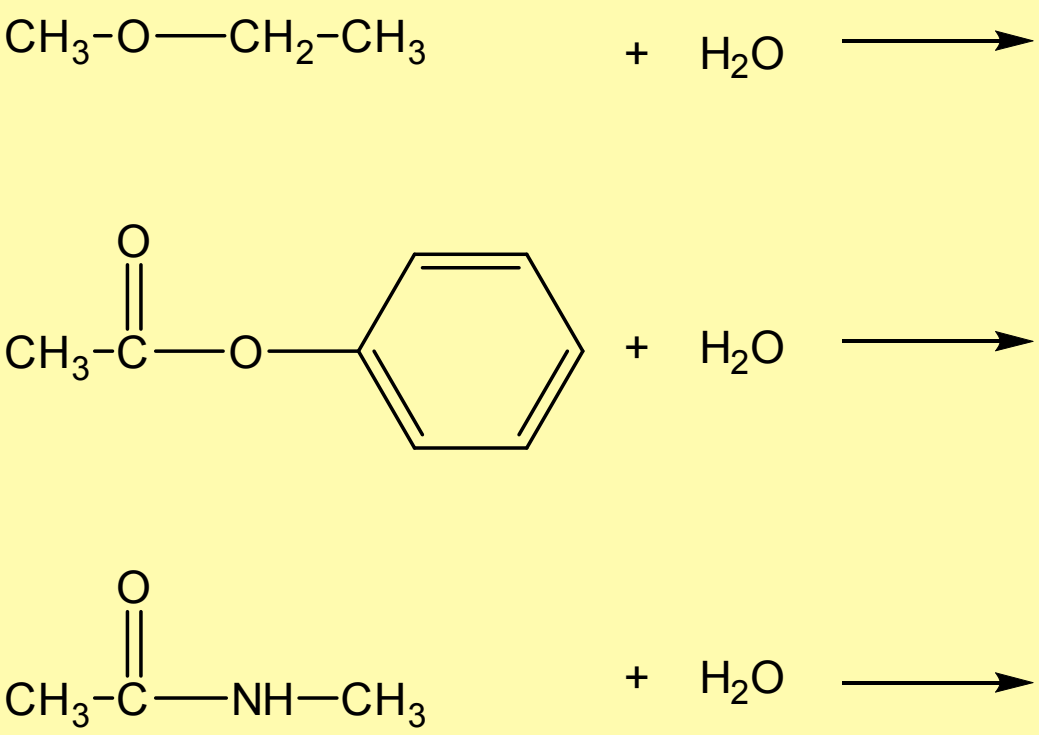


Try It!

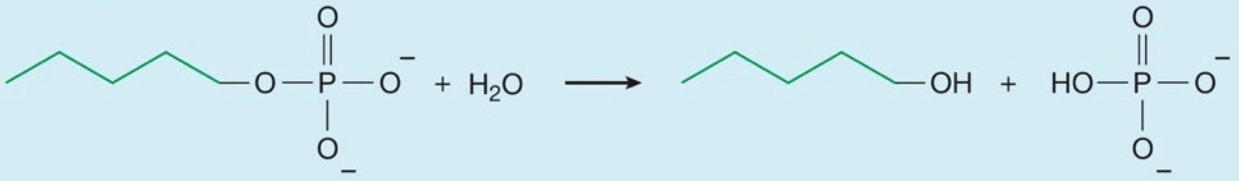
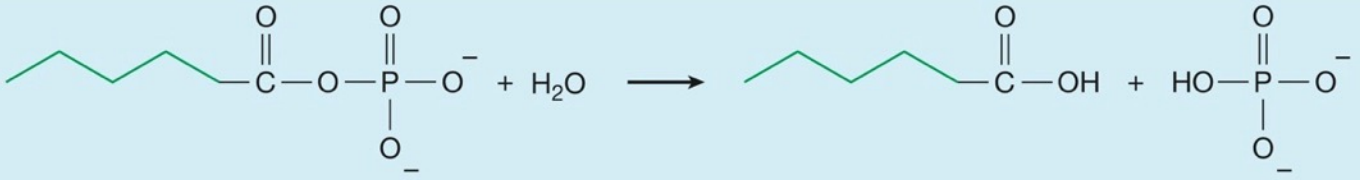
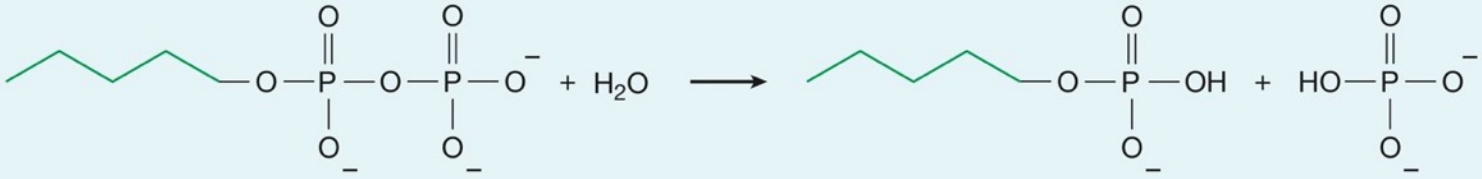
Question:

Complete the following hydrolysis reactions.



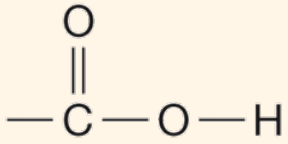
Important Hydrolysis Reactions in Biochemistry

TABLE 13.2 Other Important Hydrolysis Reactions in Biochemistry

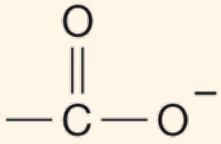
Functional Group	Hydrolysis Reaction
Phosphoester	
Thioester	
Phosphoric anhydride	
Diphosphate	

13.5 The Effect of pH on Products of Hydrolysis

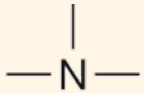
- Most of the hydrolysis reactions we have learned produce either a carboxylic acid or an amine (or both!)
- Under physiological conditions (near pH 7), both of these will undergo ionization.



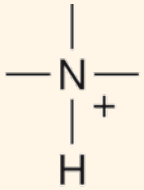
Carboxylic acid functional group



pH 7 form of a carboxylic acid (carboxylate ion)



Amine functional group



pH 7 form of an amine (alkylammonium ion)

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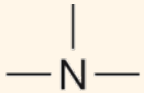
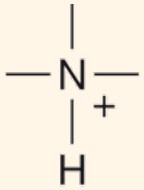
Carboxylic acid functional group

pH 7 form of a carboxylic acid (carboxylate ion)



Amine functional group



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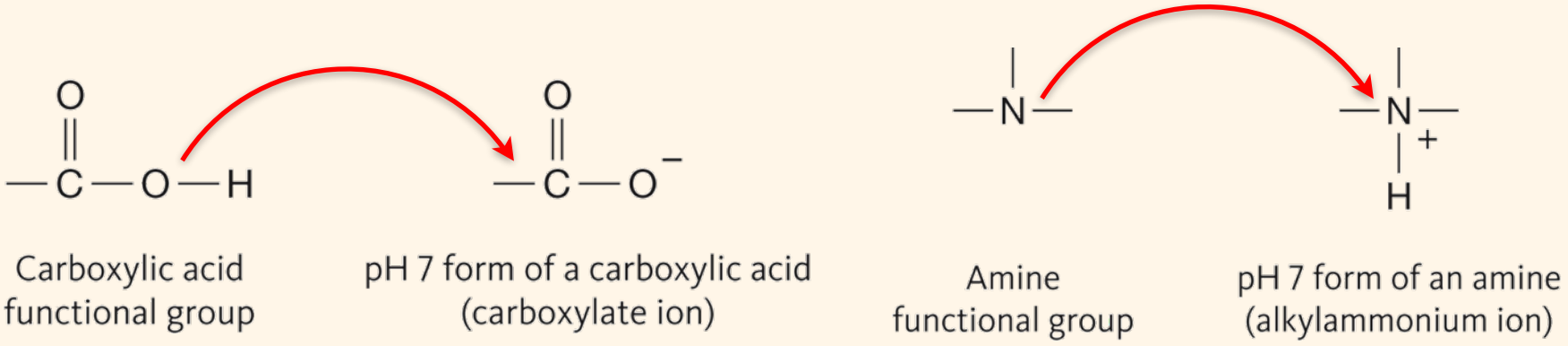
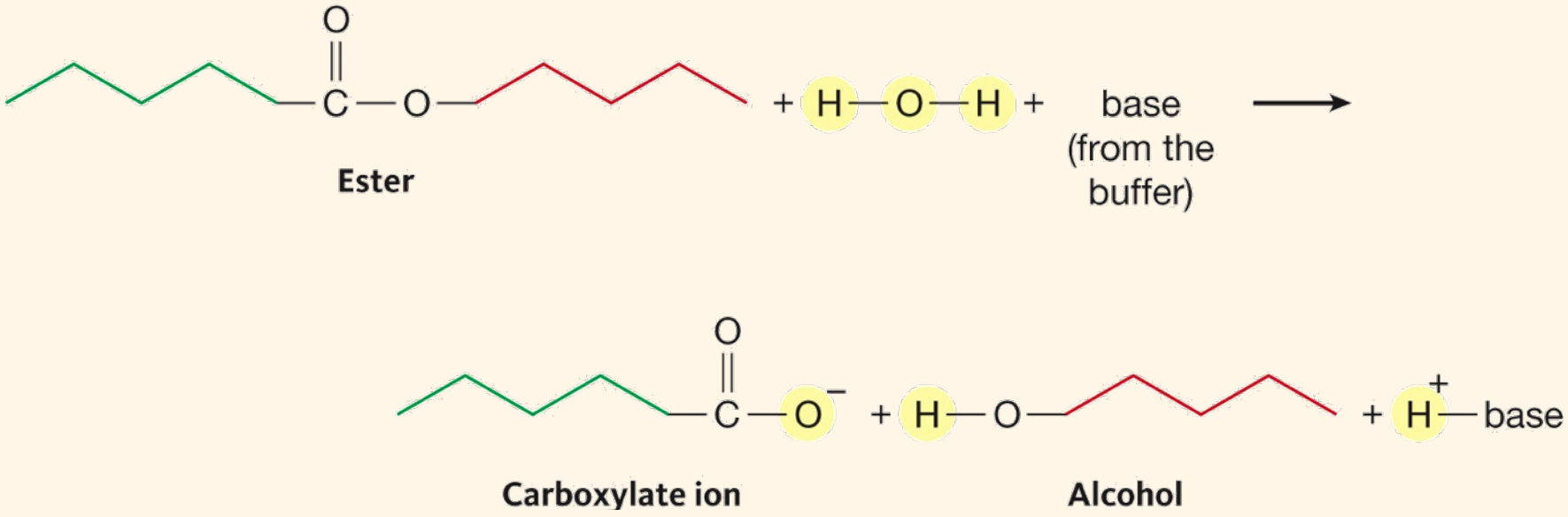


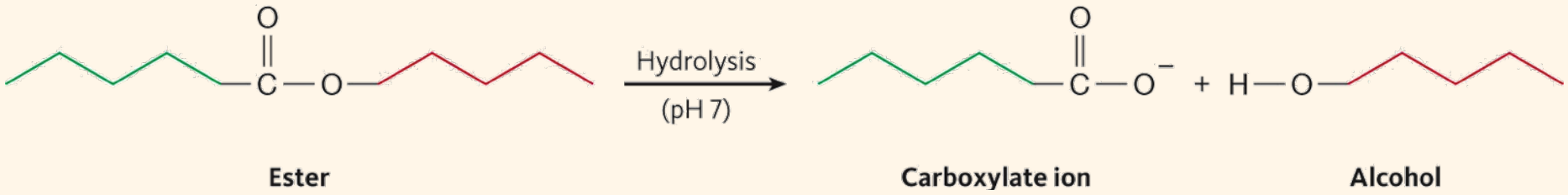
Ester Hydrolysis at pH 7

- When buffered at pH 7, ester hydrolysis produces an alcohol, a carboxylate ion and a protonated base (from the buffer)
- The basic component of the buffer removes the H^+ from the original carboxylic acid.



Simplified Reaction

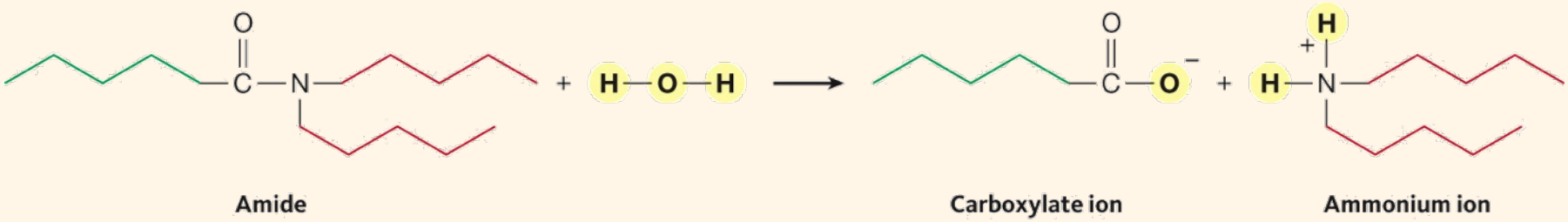
- Often this type of reaction is simplified only to show the organic products.



- The alcohol does not ionize because it is not acidic!

Amide Hydrolysis at pH 7

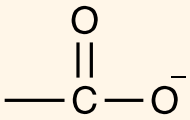
- Because the amine produced in amide hydrolysis will accept H^+, there is no need to include a base from the buffer in the reaction.

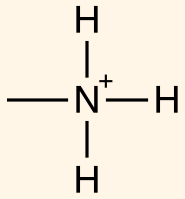


Functional groups at pH 7

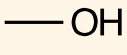
- At *pH7*, carboyxlic acids switch to their ionized carboxylate forms and amines switch to their ionized ammonium form.
- Alcohols and thiols are unionized at *pH* 7.

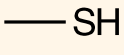
ionized





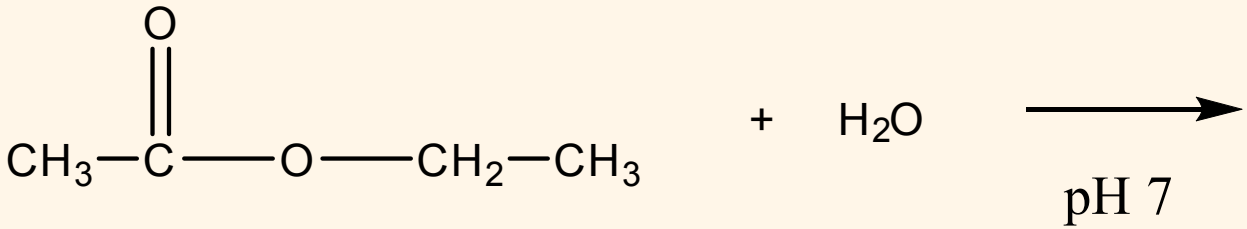
unionized

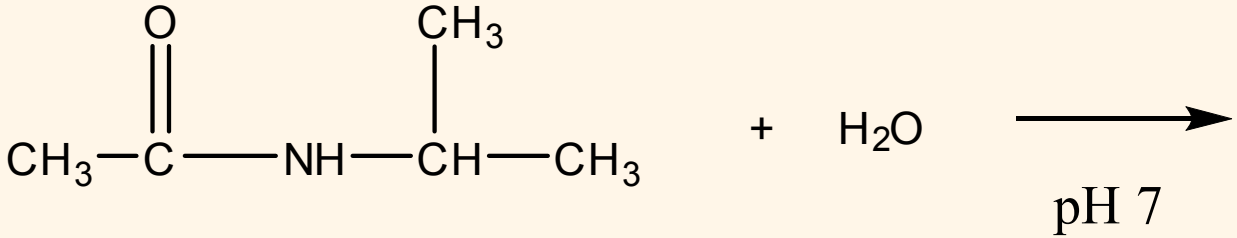




Try It!

- Draw the structures that are formed in the following hydrolysis reactions buffered at pH 7.

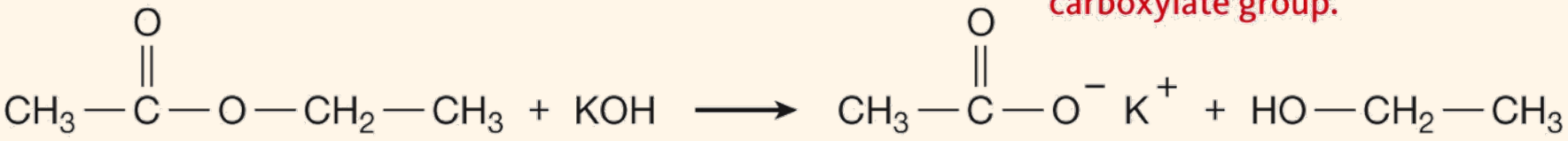




Esters Hydrolyzed by Strong Bases

- Strong bases such as KOH and NaOH are often used as catalysts in ester hydrolysis.
- These bases remove the H^+ from the carboxylic acid as it forms, and the cation (K^+ or Na^+) will associate with the carboxylate ion forming a carboxylate salt.

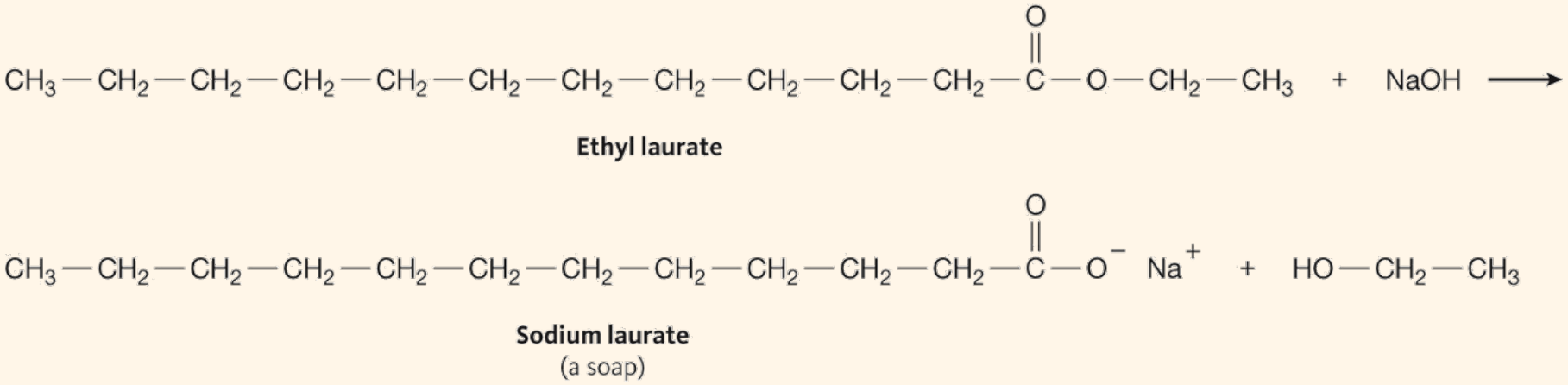
In structural formulas of carboxylate salts, we draw the metal ion beside the carboxylate group.



Ethyl acetate (an ester) + **Potassium hydroxide** (a strong base) → **Potassium acetate** (a carboxylate salt) + **Ethanol** (an alcohol)

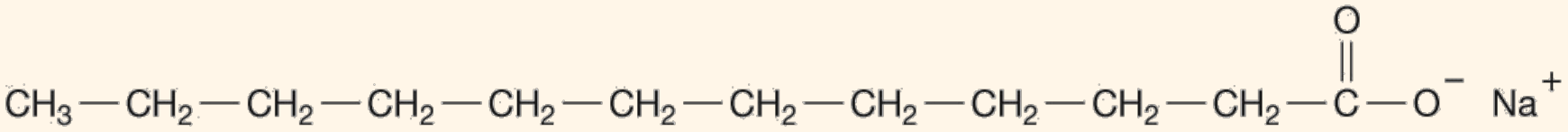
Saponification Reactions

- The reaction of an ester with a strong base is often called a saponification ("soap-forming" reaction).
- Soaps contain long chain carboxylate salts, like sodium laurate.



Saponification Reactions

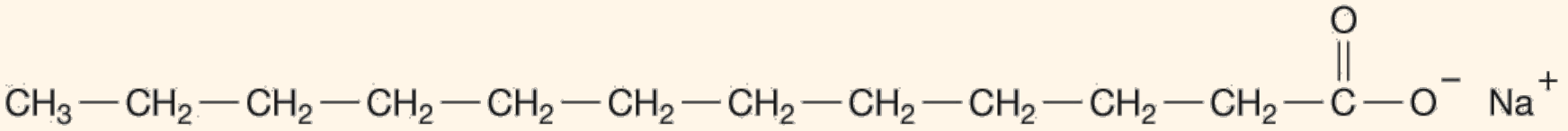
- Soaps form **micelles**, when placed in water



Sodium laurate
(a soap)

Saponification Reactions

- Soaps form **micelles**, when placed in water



Sodium laurate
(a soap)

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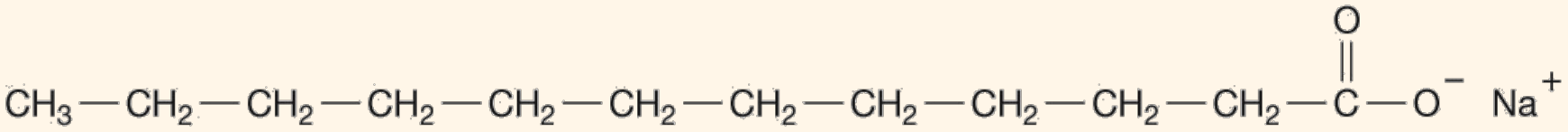
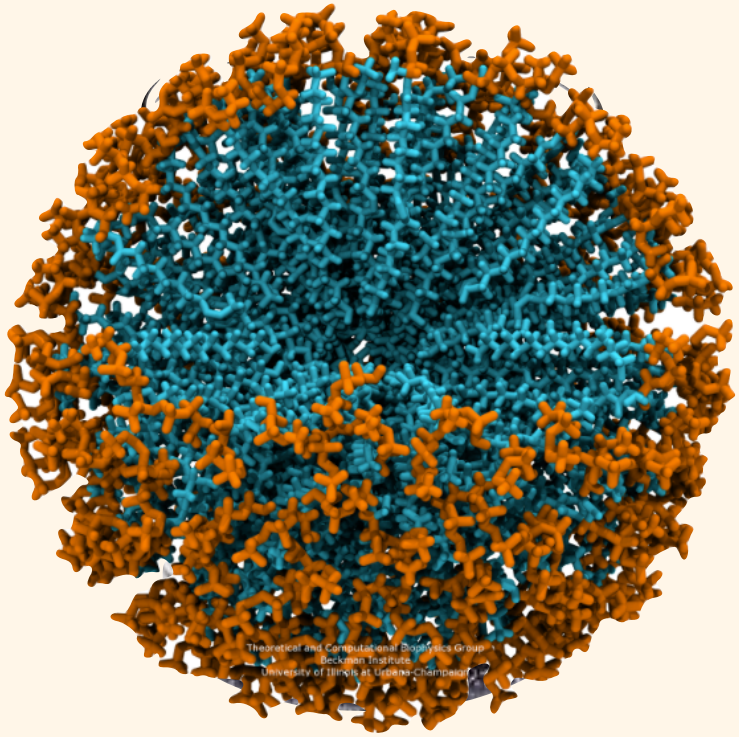


Sodium laurate
(a soap)



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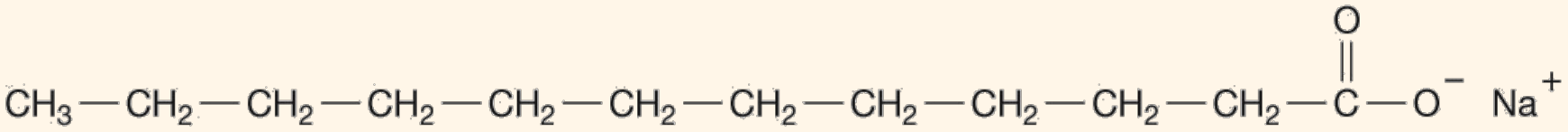
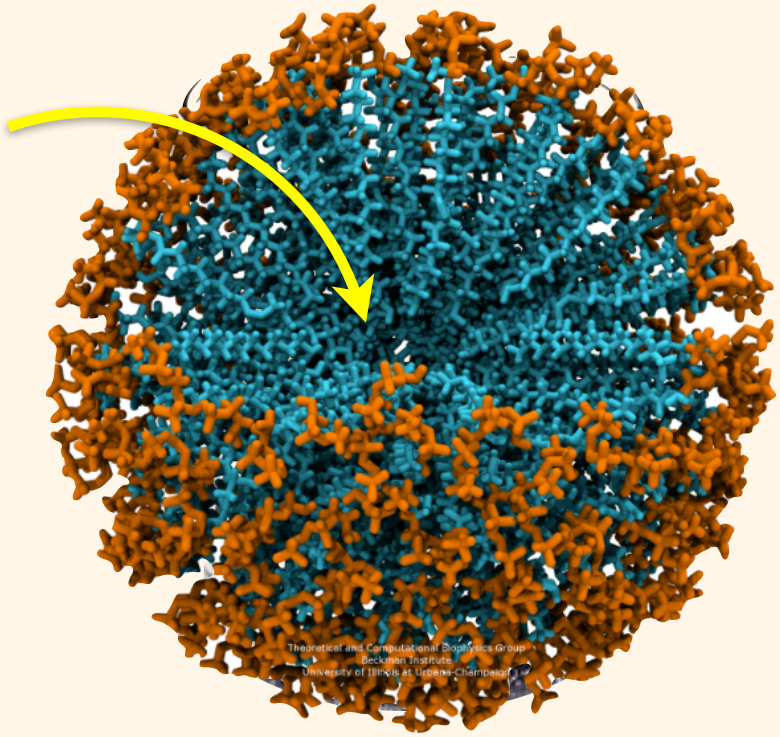


Sodium laurate
(a soap)

grease on the inside

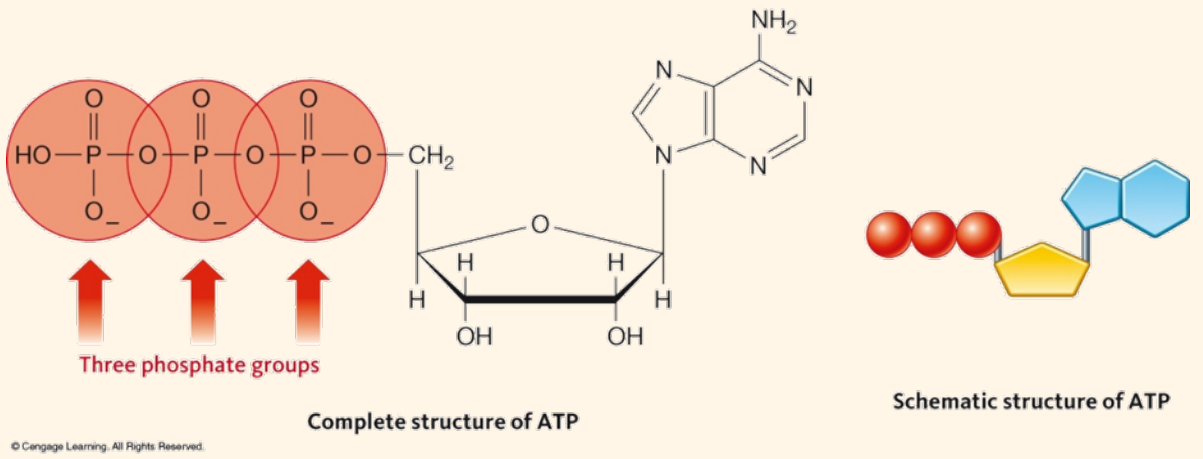
and

water on the outside



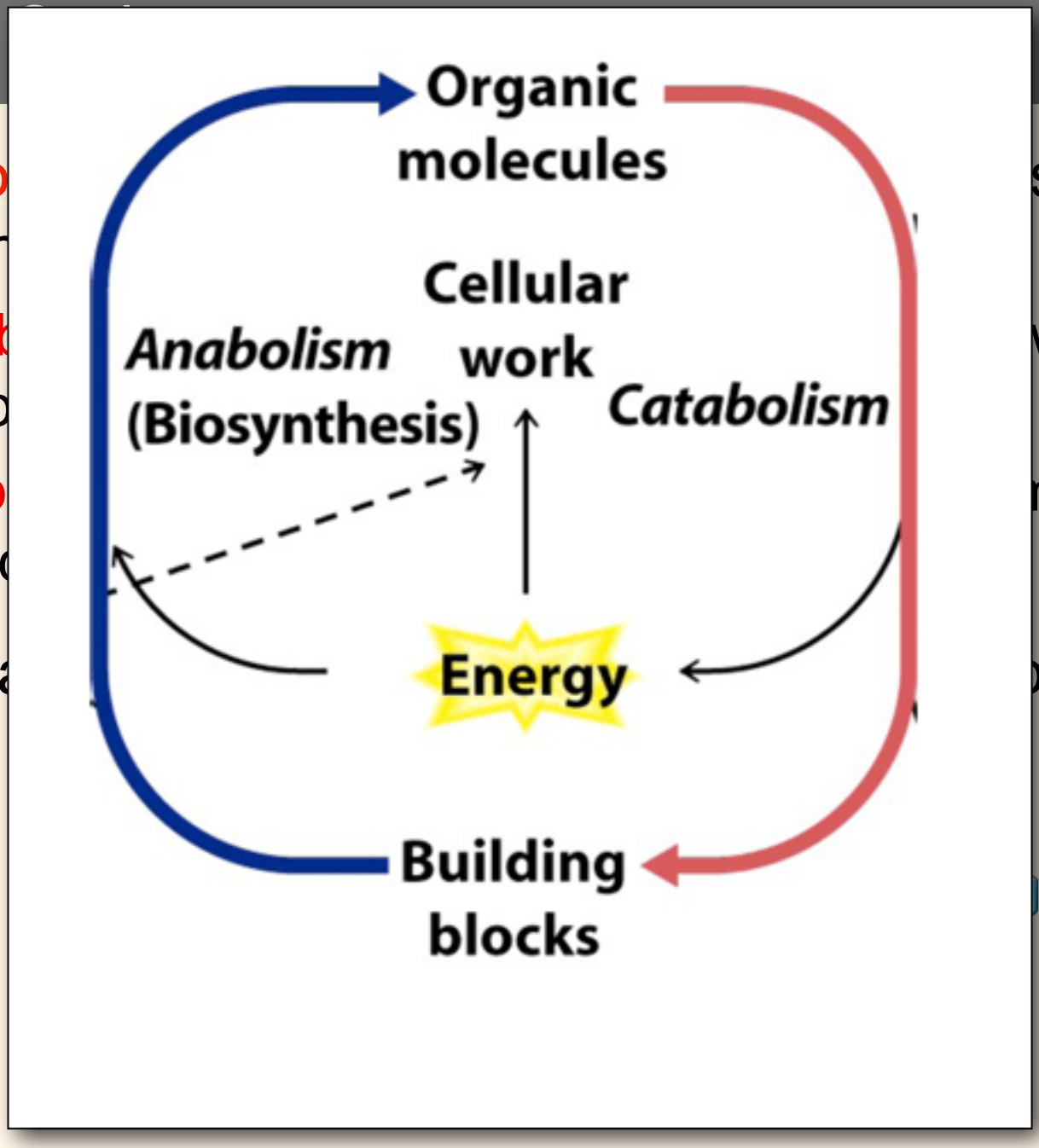
13.6 ATP Cycle

- Metabolism is the sum of all chemical processes that occur in an organism.
  - Catabolism: produces energy and breaks down complex molecules into simpler ones.
  - Anabolism: consumes energy and builds complex molecules from simpler ones.
- ATP is a link between catabolism and anabolism



13.6 ATP

- Metabo… …sses that occur in…
  - Catab… …wn comp…
  - Anab… …nplex molec…
- ATP is a… …olism



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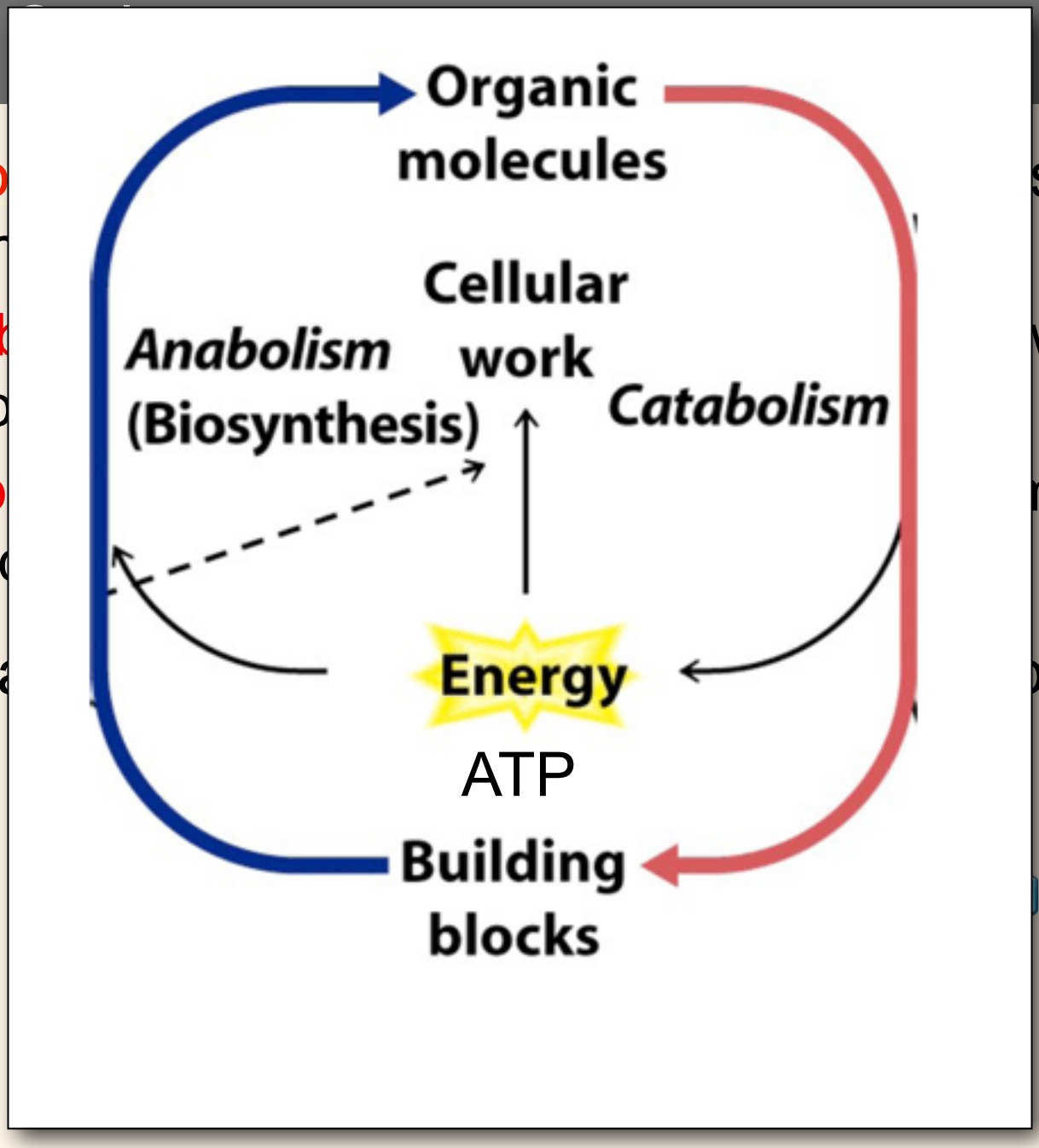

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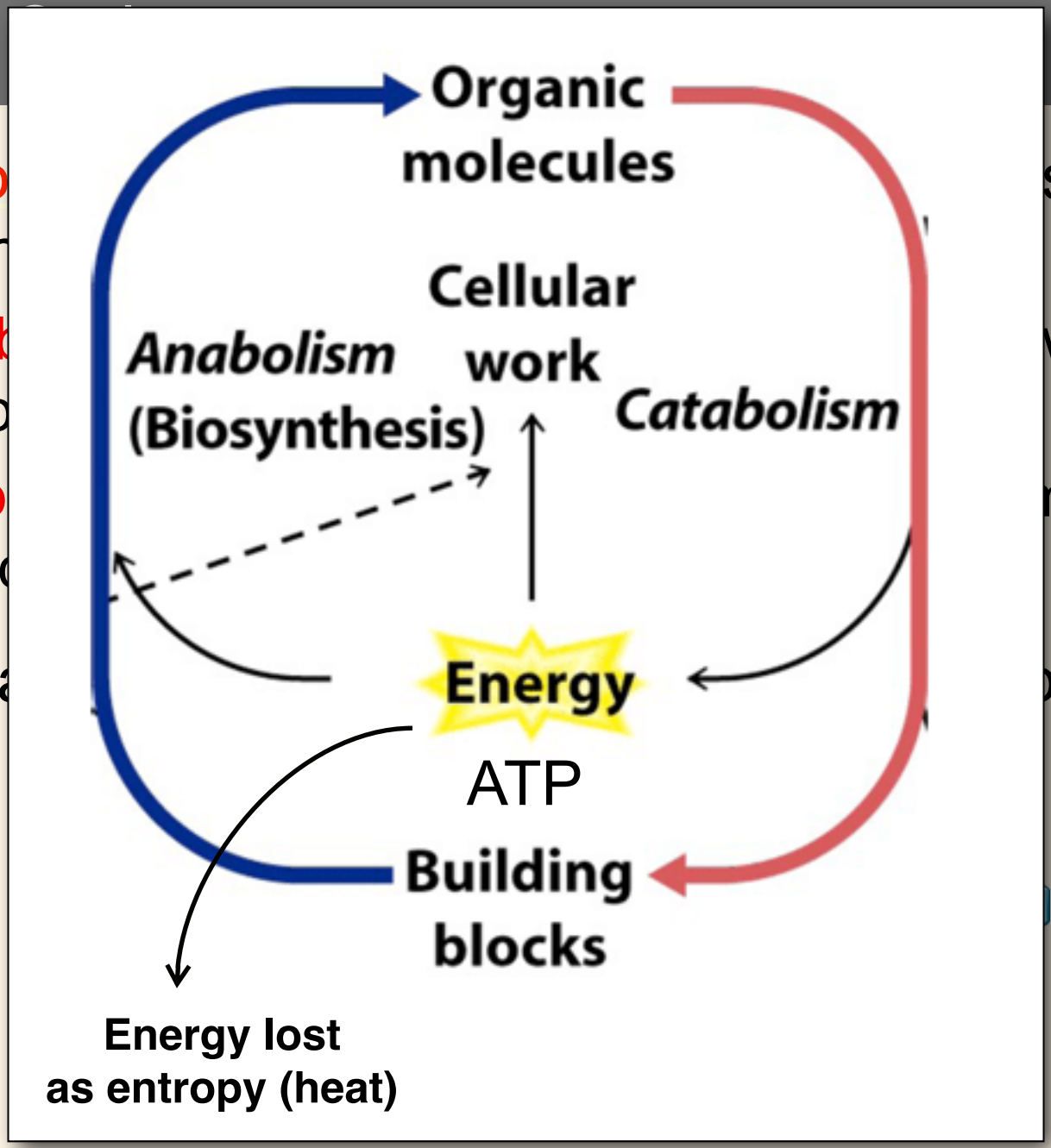

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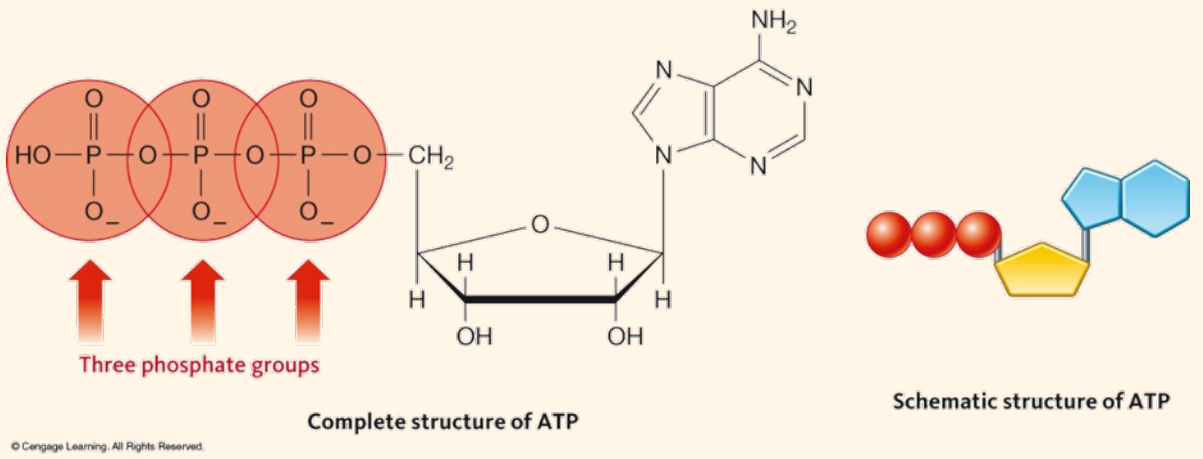
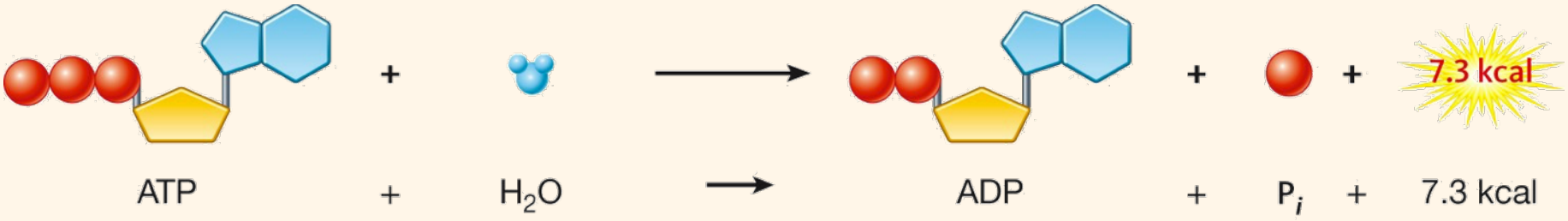


Hydrolysis of ATP

- ATP hydrolysis releases energy
  - 7 kcal of energy are released for every mole of phosphate groups that is hydrolyzed.
- P_i is an inorganic phosphate ion



Energy

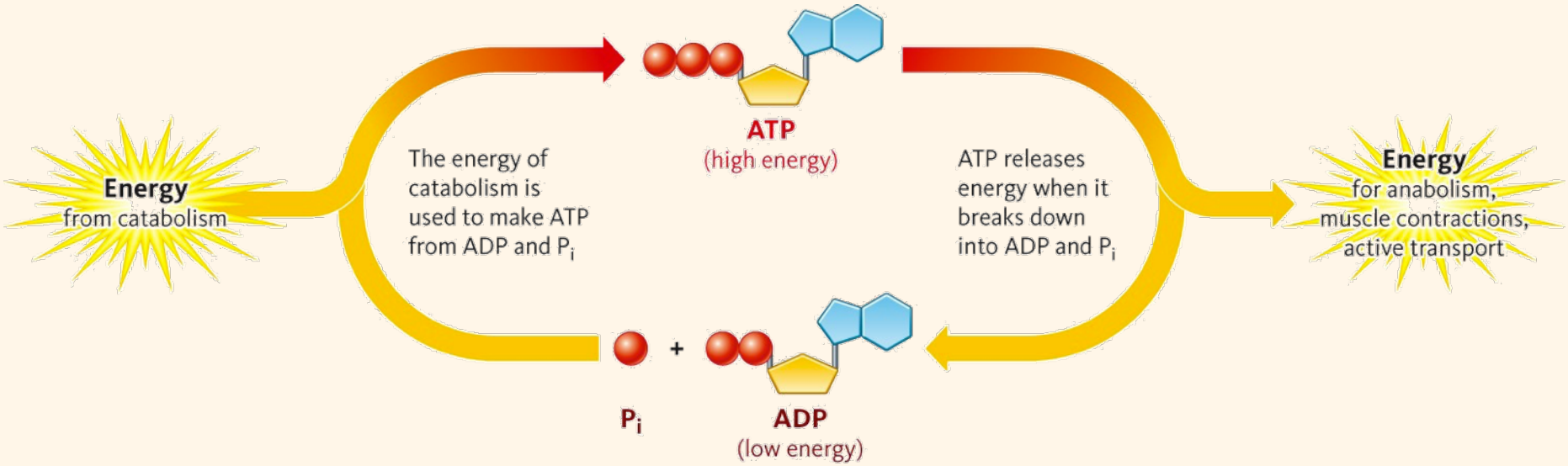
- Hydrolyzing ATP into ADP (adenosine diphosphate) and inorganic phosphate ion (P_i) releases 7.3 kcal/mol.

$ATP + H_2O \rightarrow ADP + P_i + 7.3\ kcal/mol$ (Exothermic)

- Conversely, producing ATP from ADP and P_i requires 7.3 kcal/mol.

$ADP + P_i + 7.3\ kcal/mol \rightarrow ATP + H_2O$ (Endothermic)

ATP Cycle


Energy
from catabolism
The energy of catabolism is used to make ATP from ADP and P_i
ATP
(high energy)
ATP releases energy when it breaks down into ADP and P_i
Energy
for anabolism, muscle contractions, active transport
+
P_i
ADP
(low energy)

Energy from Glucose

- The number of ATP molecules produced in a specific pathway are a measure of the pathway's ability to produce energy.

Lactic Acid Fermentation:

glucose → lactic acid (produces 2 ATP)

Complete Oxidation of Glucose:

glucose + 6 O_2 → 6 CO_2 + 6 H_2O (produces 32 ATP)

Other processes

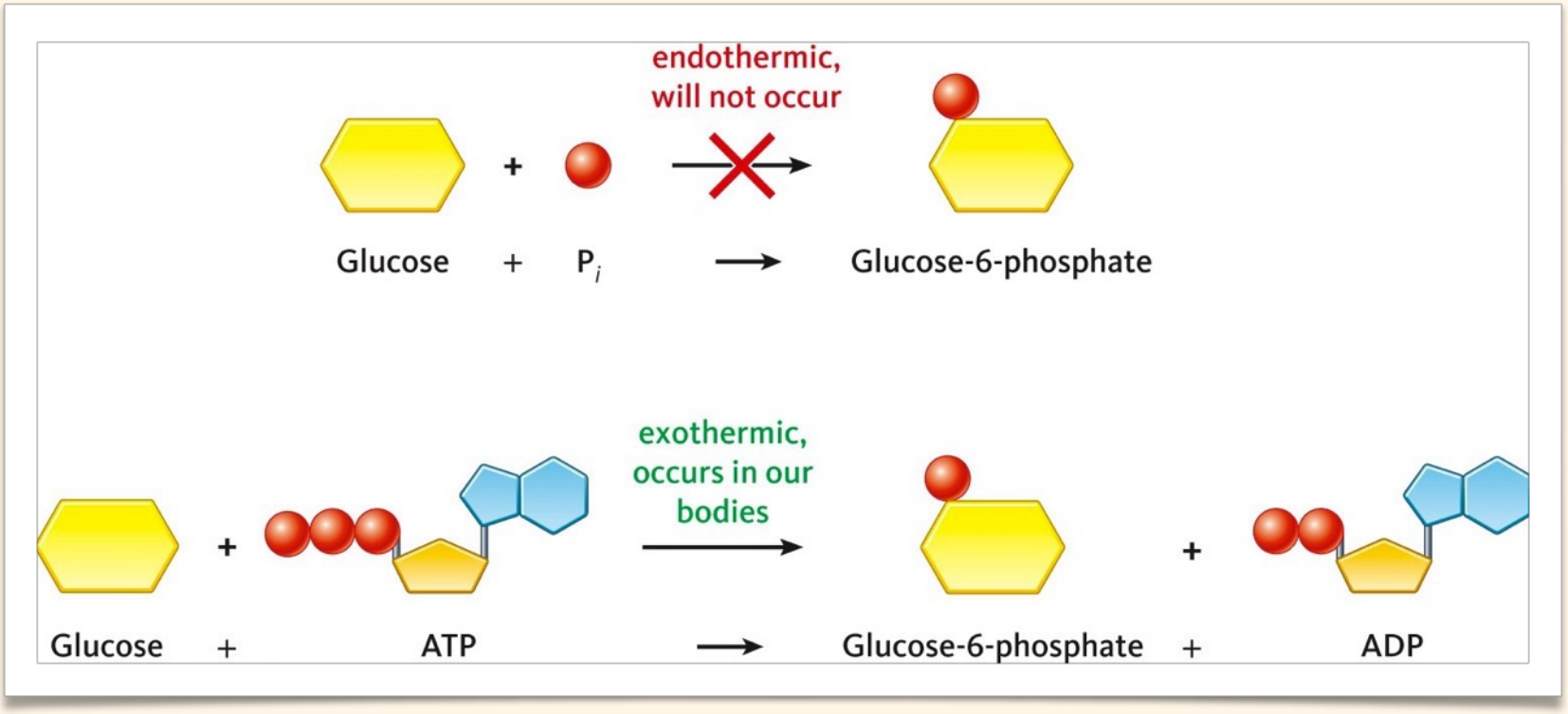
ATP is used in many processes:

- Phosphorylating other molecules
- Supplying energy for other reactions
- Supplying energy for muscle contractions
- Supplying energy for “upstream” membrane transport

Other processes

ATP is used in many processes:

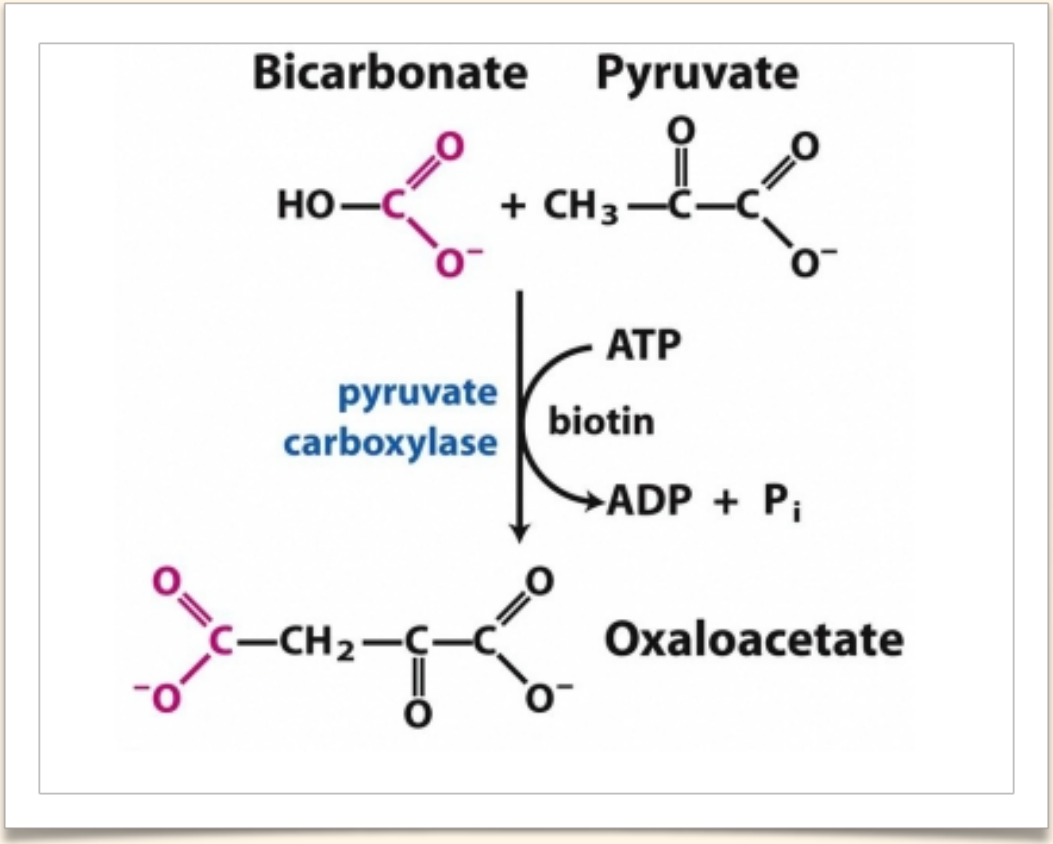
- Phosphorylating other molecules



Other processes

ATP is used in many processes:

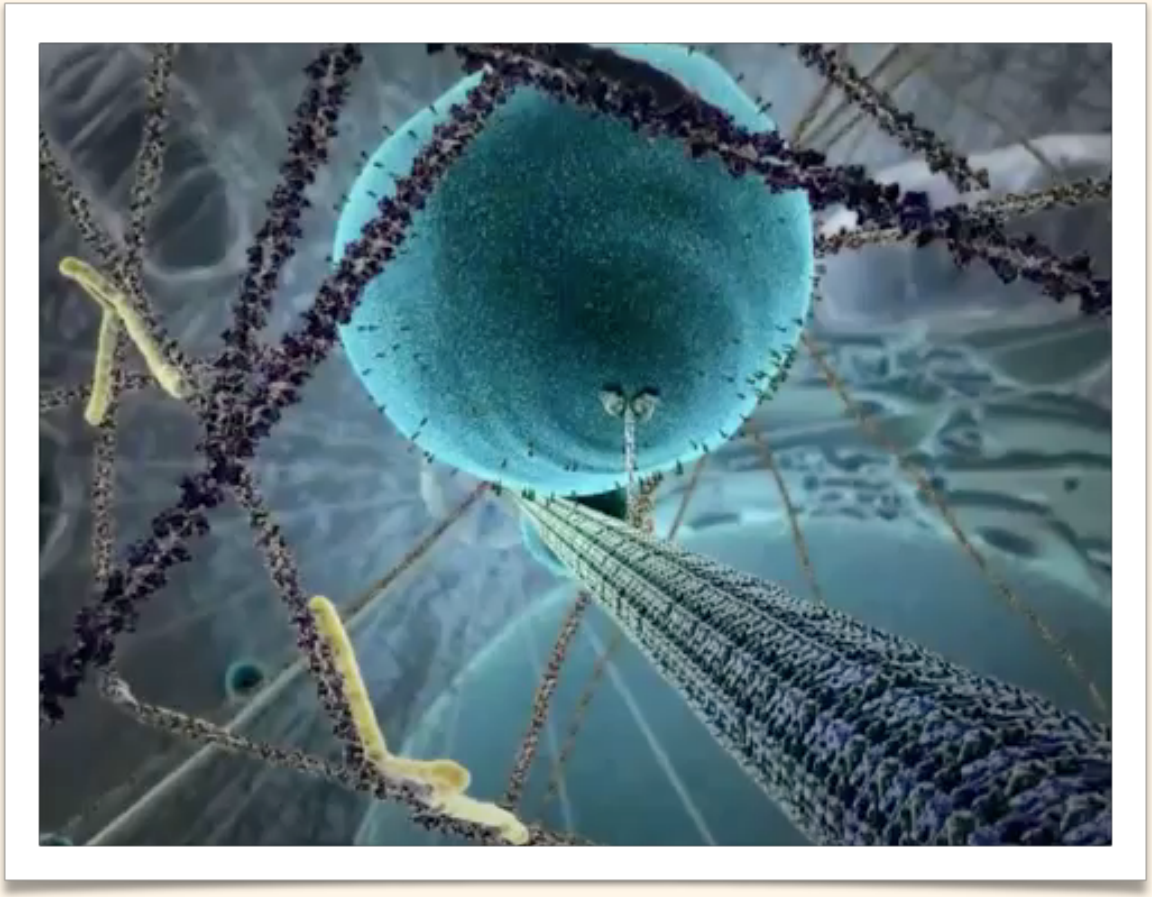
- Supplying energy for other reactions



Other processes

ATP is used in many processes:

- Supplying energy for mechanical movement



Other processes

ATP is used in many processes:

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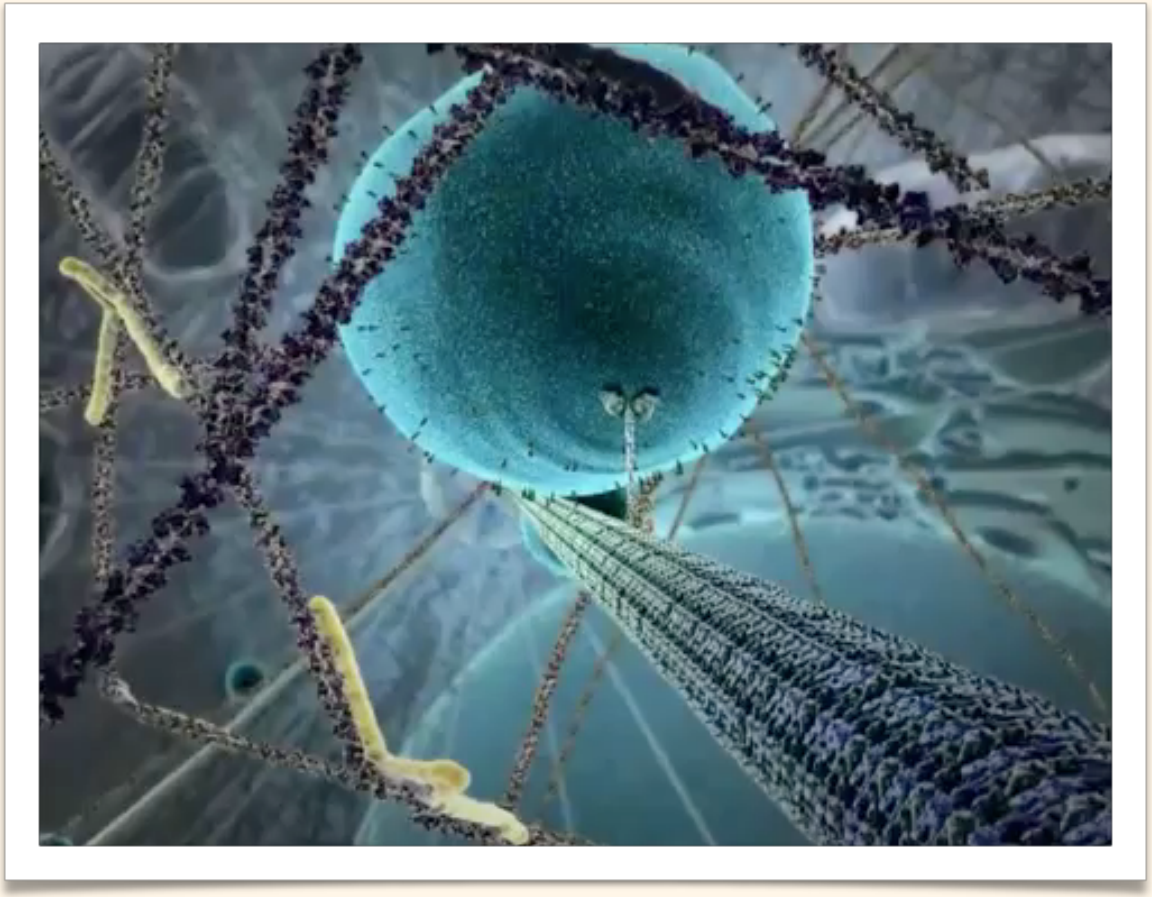
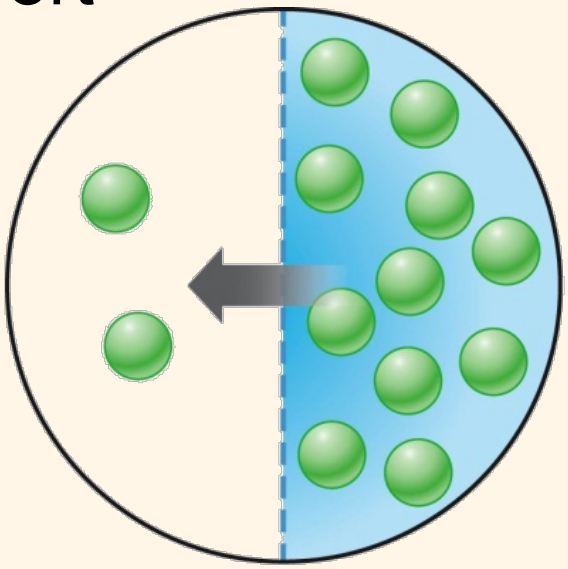


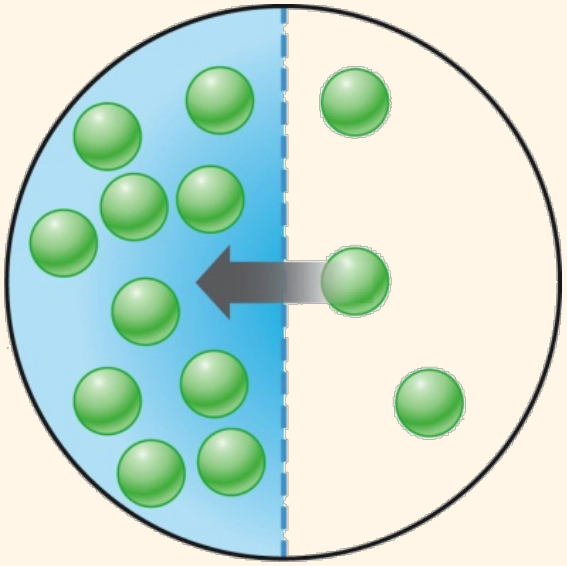
Other processes

ATP is used in many processes:

- Supplying energy for “upstream” membrane transport



Solute particles move from high concentration to low concentration (normal direction of diffusion) – **no energy required**



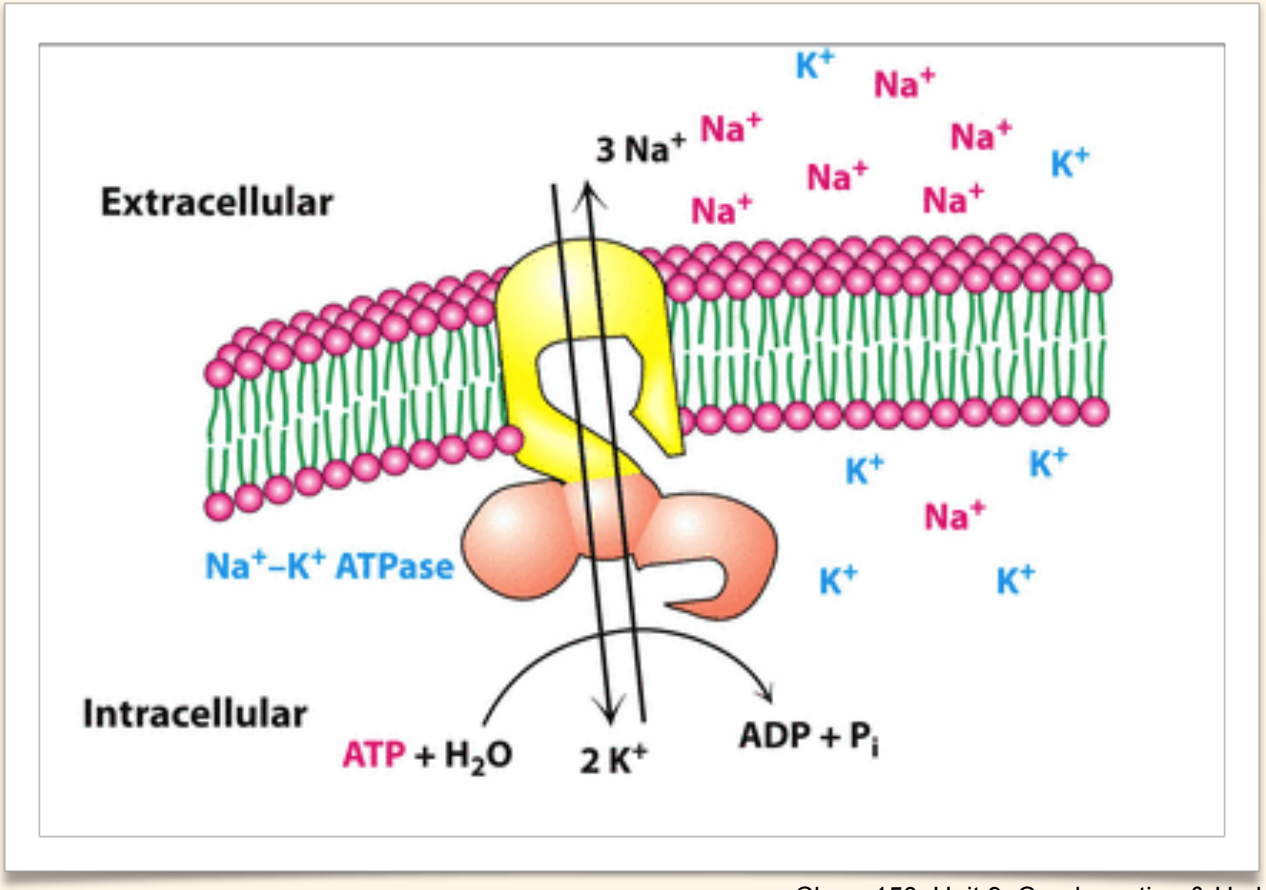
Solute particles move from low concentration to high concentration – **requires energy from ATP hydrolysis**

Other processes

ATP is used in many processes:

- Supplying energy for “upstream” membrane transport

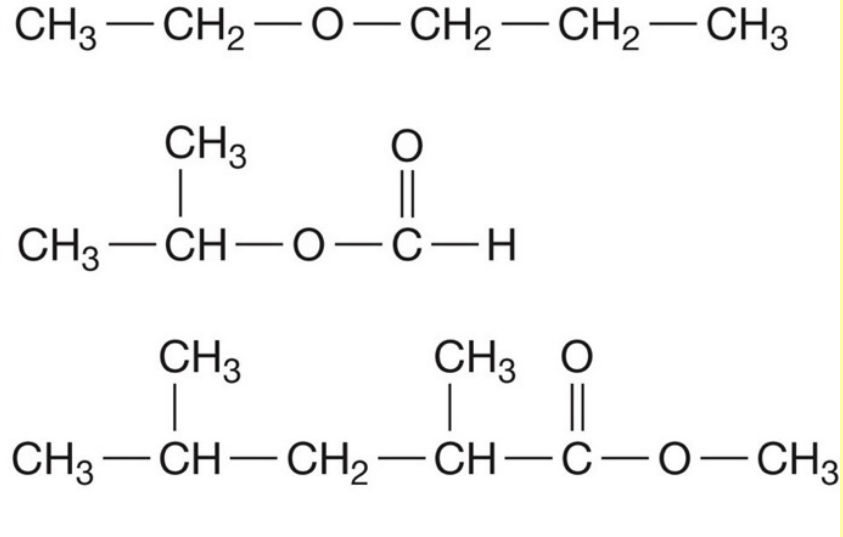
Na^+-K^+ pump

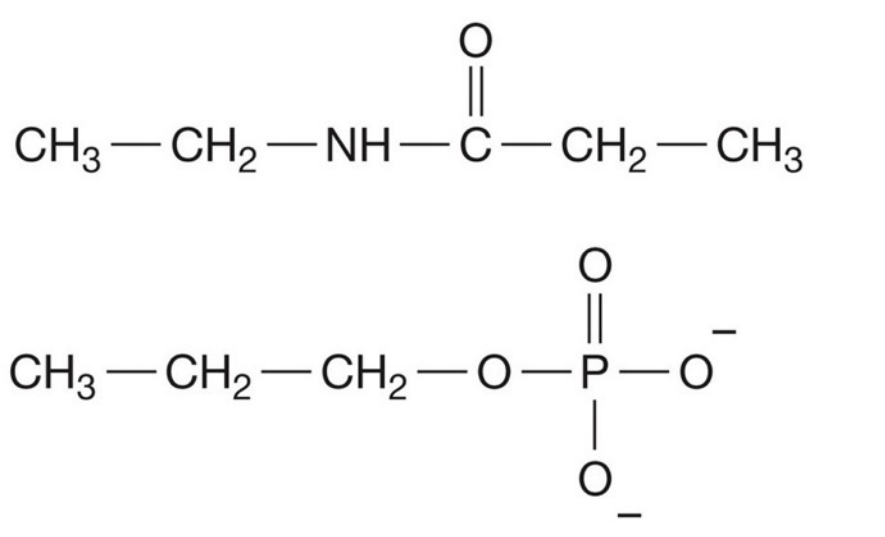


Try It!

Question:

Use structural formulas to complete the following hydrolysis reactions?





Next Up

- Unit 10: Proteins
  - Unit 10 Assignments due 14. April (deadline 21. April)