American Chemical Society

ACS Chemistry for Life®

USNCO Coaching Session Local Section Exam Preparation Tutorial Notes: Organic/Biochemistry

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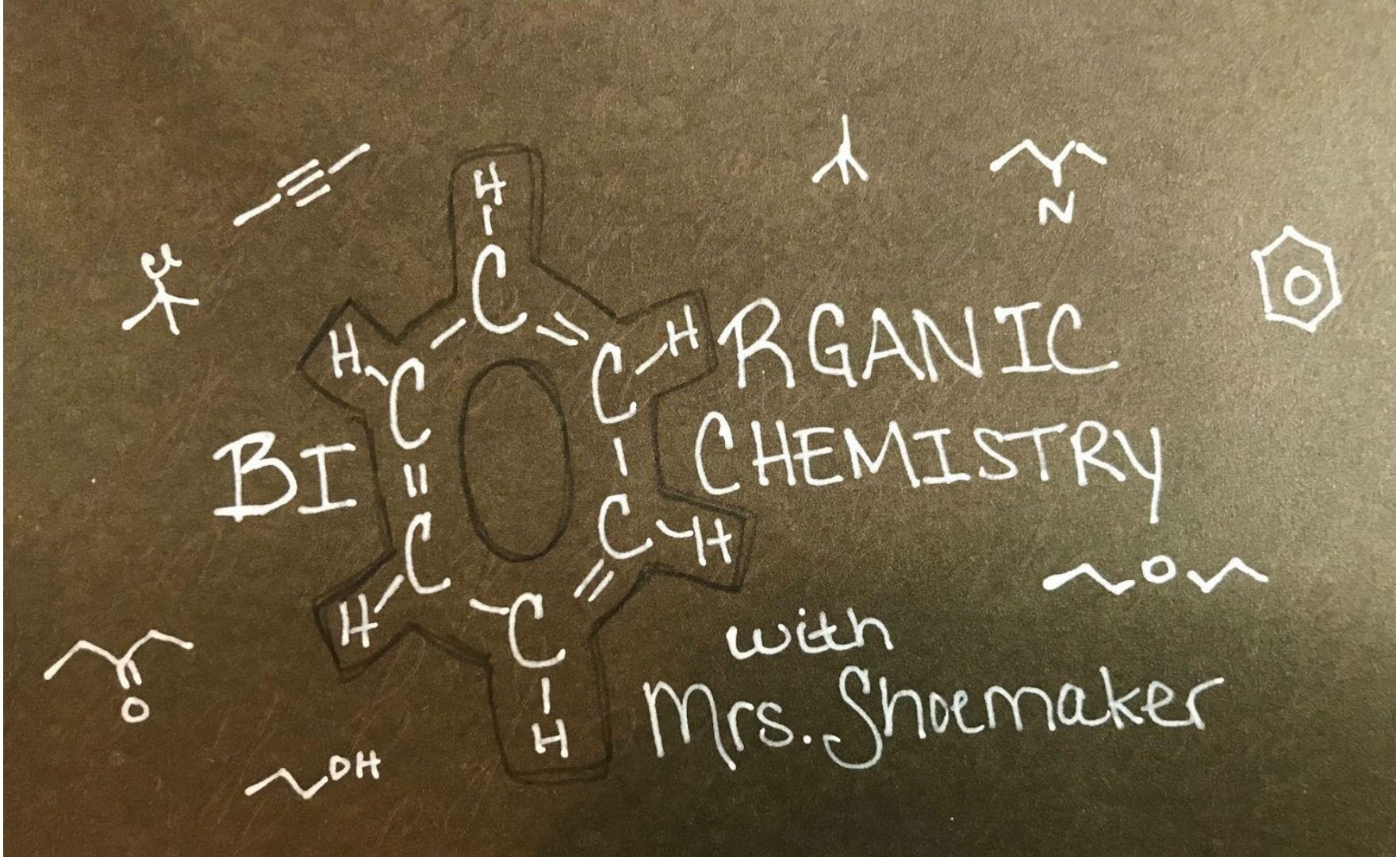

BIORGANIC
CHEMISTRY
with
Mrs. Shoemaker

Definitions

Organic Chemistry

The branch of chemistry which deals with the study of compounds of carbon and hydrogen (hydrocarbons) and their derivatives.

Biochemistry

The branch of chemistry which deals with the chemistry and chemical compounds of living organisms.

Nomenclature - Organic Chemistry

- The nomenclature of organic compounds is a set of directions designed to recreate the structure of the molecule using prefixes and suffixes. The longest continuous chain of carbon in a compound is considered the parent chain and the name begins with the information that will tell us how many carbon (numeric prefix) and the type of bonds that exist between the carbon (suffix). Additional prefixes maybe added to address substituents and suffixes for the main functional group. Numbers are used in the name to describe the location of the attachments and/or double and triple bonds.

Prefixes:

Notice the prefixes do not have a vowel ending, this is important because the vowel will come from the suffix.

• Meth = 1	methane (gas burned by a bunsen burner)
• Eth = 2	
• Prop = 3	propane (gas burned by a BBQ gas grill)
• But = 4	
• Pent = 5	
• Hex = 6	
• Hep = 7	
• Oct = 9	octane (found in gasoline)
• Dec = 10	
• Undec = 11	
• Dodec = 12	

Suffixes and General Formulas:

	Suffix	General Formula	
Alkanes - carbons are connected by single bonds	**-ane**	C_nH_{2n+2}	
Alkenes - carbon connections contain at least one double bond	**-ene**	C_nH_{2n}	**Subtract 2 add'l H for each additional double bond**
Alkynes - carbon connections contain at least one triple bond	**-yne**	C_nH_{2n-2}	**Subtract 4 add'l H for each additional triple bond**

Aliphatic = parent chain is "straight"
Alicyclic = parent chain is in a ring formation

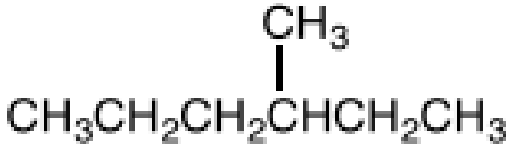
Alkyl Branches

- Practice:
  - 4-chloro-2-methylheptane
  - 2-bromocyclopentene

Alkyl Group	Structure
methyl	CH_3-
ethyl	CH_3CH_2-
n-propyl	$CH_3CH_2CH_2-$
isopropyl	CH_3CHCH_3 (CH bonded to two CH$_3$)
n-butyl	$CH_3CH_2CH_2CH_2-$
sec-butyl	$CH_3CH_2CHCH_3$ (CH bonded to CH$_2$CH$_3$ and CH$_3$)
isobutyl	CH_3CHCH_2- with CH_3 branch
tert-butyl	CH_3CCH_3 with CH_3 branch

2018 National Exam

55. Which statement about the branched hydrocarbon shown is correct?



(A) Its IUPAC name is 4-methylhexane.

(B) It is chiral.

(C) It has six primary hydrogens.

(D) Radical chlorination gives 1-chloro-4-methylhexane as the major product.

Properties of Hydrocarbons

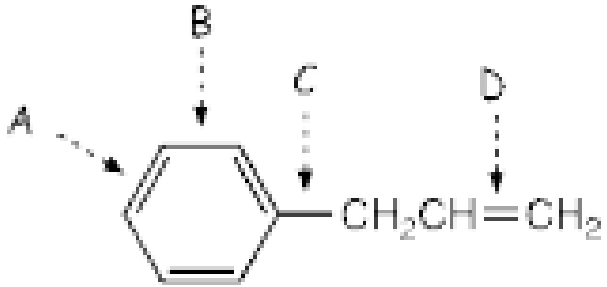
- Non-polar
- Generally low boiling points at Room Temperature
- Boiling points increase as the number of carbon increase
- Boiling points decrease as the number of branches increase (with a constant number of carbon)
- 1st four are gases at room temperature (methane, ethane, propane, butane)
- Densities are generally less than 1 g/ml
- Bond lengths:
  - longest - single C-C
  - double bond in aromatic (due to resonance)
  - double bond
  - shortest - triple bond

Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)
methane	CH_4	–182.5	–161.5
ethane	C_2H_6	–183.3	–88.6
propane	C_3H_8	–187.7	–42.1
butane	C_4H_{10}	–138.3	–0.5
pentane	C_5H_{12}	–129.7	36.1
hexane	C_6H_{14}	–95.3	68.7
heptane	C_7H_{16}	–90.6	98.4
octane	C_8H_{18}	–56.8	125.7
nonane	C_9H_{20}	–53.6	150.8
decane	$C_{10}H_{22}$	–29.7	174.0

2020 National Exam

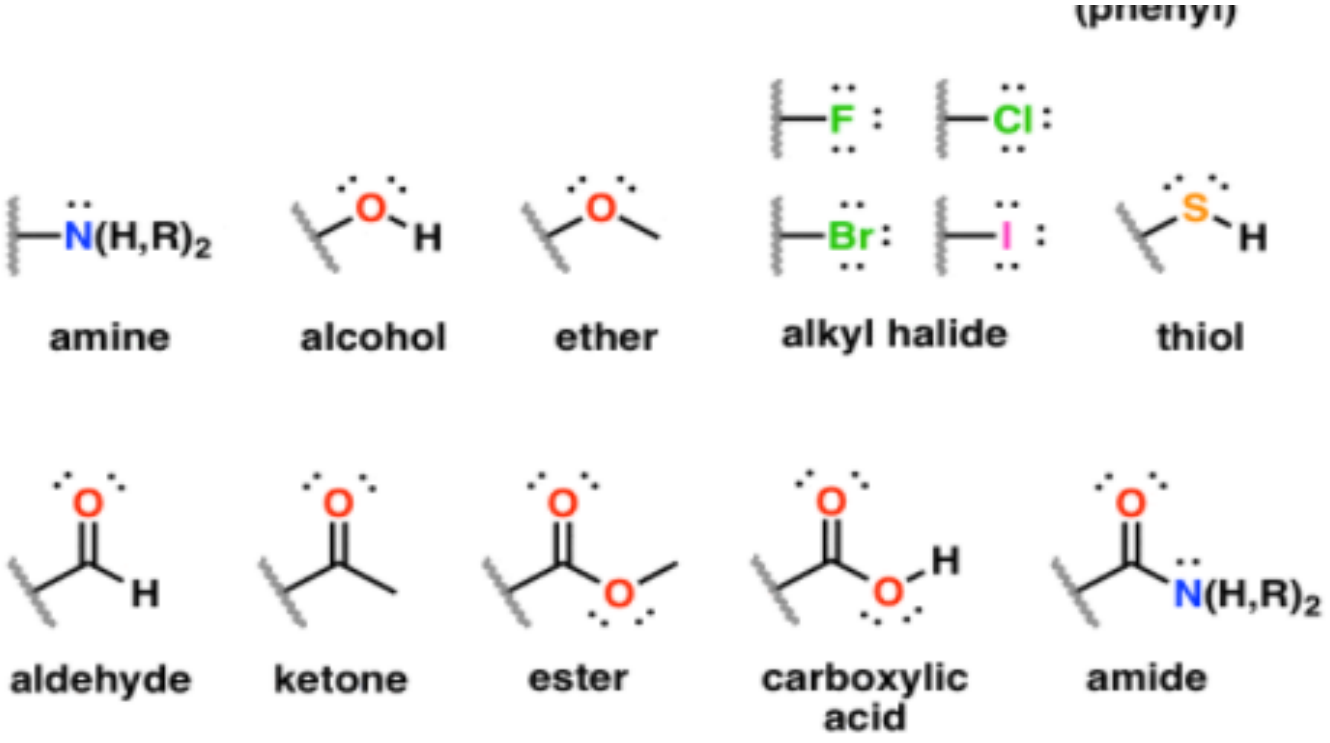
56. Which carbon-carbon bond is the shortest?



(A) A **(B)** B **(C)** C **(D)** D

Functional Groups

Groups of atoms that create unique characteristics.



Functional Group Nomenclature

Class	Suffix Name	Prefix Name
Carboxylic acid	-oic acid	Carboxy
Ester	-oate	Alkoxycarbonyl
Amide	-amide	Amido
Nitrile	-nitrile	Cyano
Aldehyde	-al	Formyl (—CH=O)
Ketone	-one	Oxo (=O)
Alcohol	-ol	Hydroxy
Amine	-amine	Amino
Alkene	-ene	Alkenyl
Alkyne	-yne	Alkynyl
Alkane	-ane	Alkyl
Ether	—	Alkoxy
Alkyl halide	—	Halo

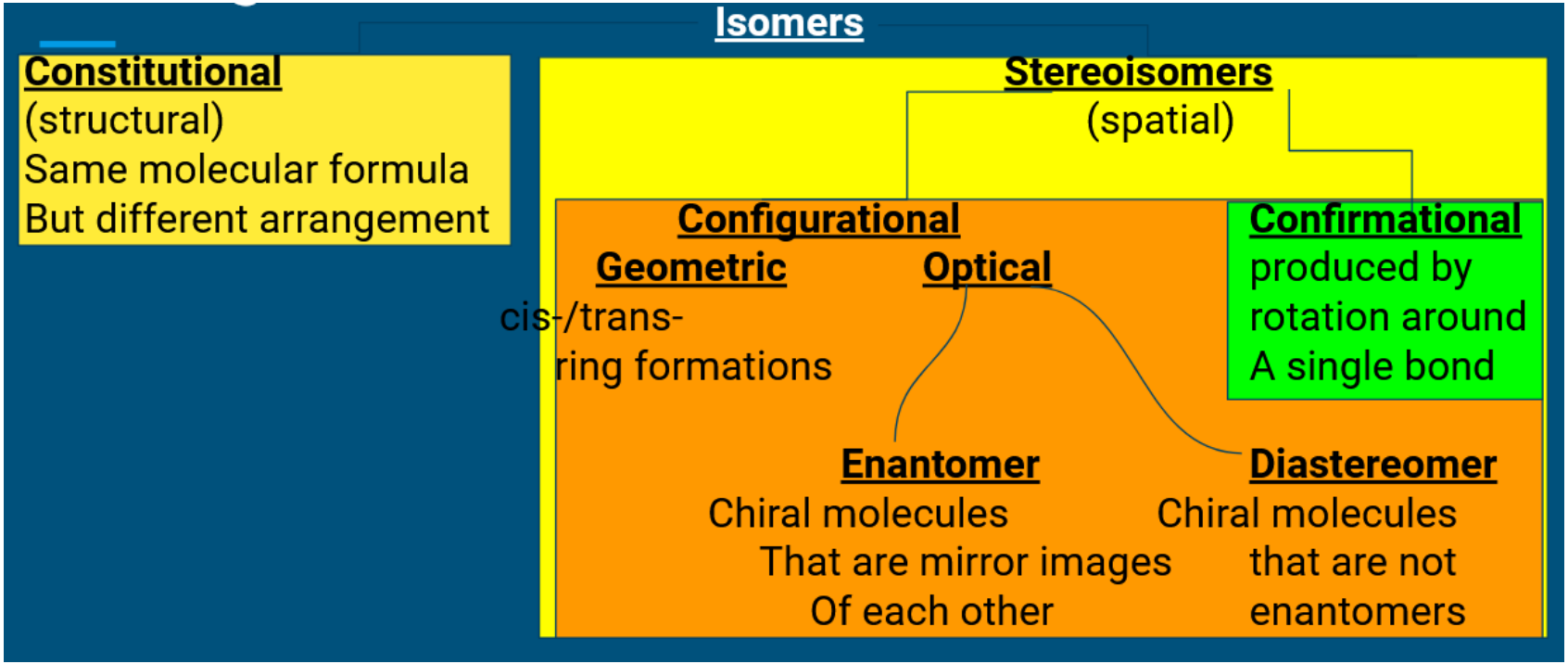
Boiling Points:

- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Water Solubility:

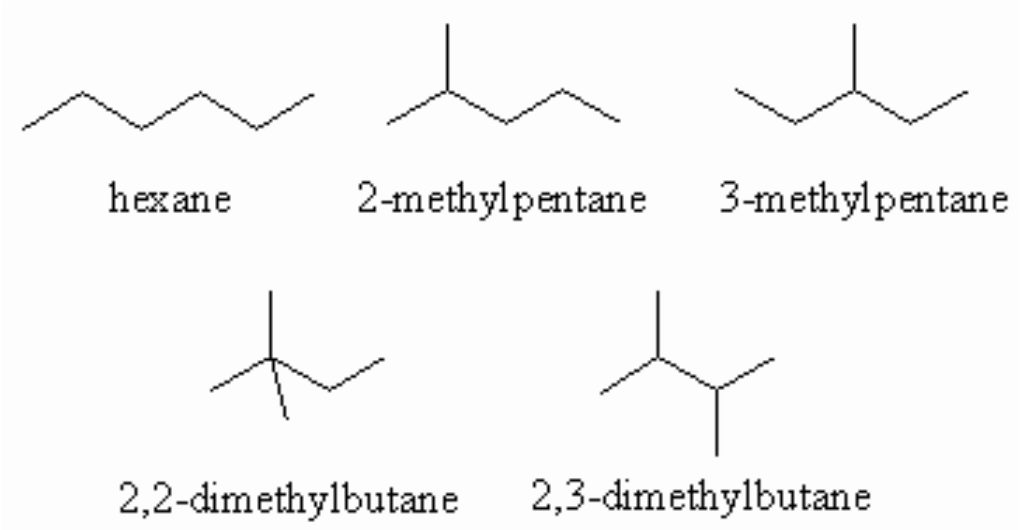
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Arrangement of Atoms Matter



Constitutional Isomers

- The molecules have the same formula, in this case C_6H_{14}, but the carbon to carbon connections are rearranged.



2016 National Exam

57. How many isomers are there with the formula C_6H_{14}?

(A) 3 **(B)** 4 **(C)** 5 **(D)** 6

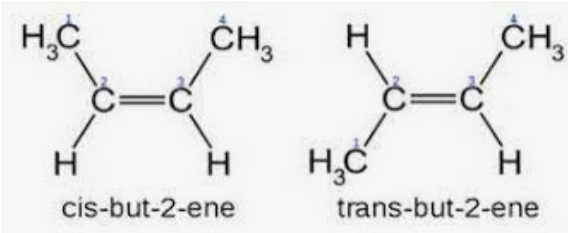
2018 National Exam

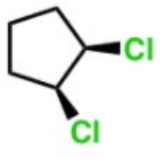
57. How many distinct acyclic compounds have the formula C_5H_{10}?

(A) 3 **(B)** 4 **(C)** 5 **(D)** 6

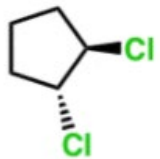
Geometric Isomers

- Isomers that are created due to a rigid structure in the molecule, generally a double bond or a ring formation.





cis-1,2-dichlorocyclopentane

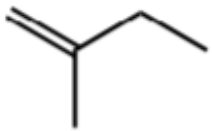


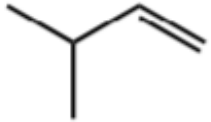
trans-1,2-dichlorocyclopentane

2021 Local Section Exam

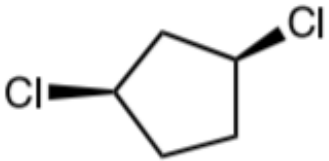
55. Which is NOT a valid representation of 3-methyl-1-butene?

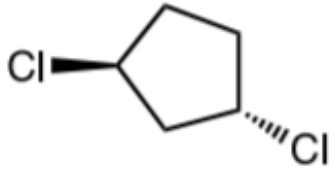
(A) $(CH_3)_2CHCH{=}CH_2$ **(B)** $CH_2CHCH(CH_3)_2$

(C) 

(D) 

56. What is the relationship between the two compounds shown?





2017 National Exam

57. (*E*)-2-butene and (*Z*)-2-butene (shown below) each react with bromine to form compounds with the formula $C_4H_8Br_2$. What is the relationship between the products?

(*E*)-2-butene

(*Z*)-2-butene

(A) Structural isomers

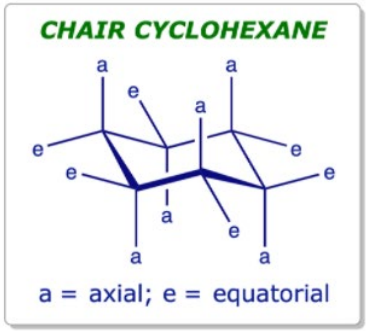
(B) Enantiomers

(C) Diastereomers

(D) Identical

Conformational Isomers

- Conformational Isomers are based on the rotation are a single bond. To the right are examples of the conformational isomers of cyclohexane.



CHAIR

C—C—C angles 111° (no angle strain)
All bonds staggered (no torsional strain)
Predominant conformation (>99.8%)

BOAT

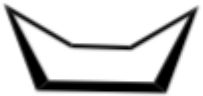
High steric strain (short 1,4 distance)
Torsional strain (eclipsing of C–H bonds)
27 kJ/mol less stable than chair

TWIST BOAT

Less steric strain than boat (1,4 distance larger)
Less torsional strain than boat (less eclipsing)
6 kJ/mol more stable than boat

2021 Local Section Exam

59. Which conformation of cyclohexane (C_6H_{12}) is most stable?

(A) 

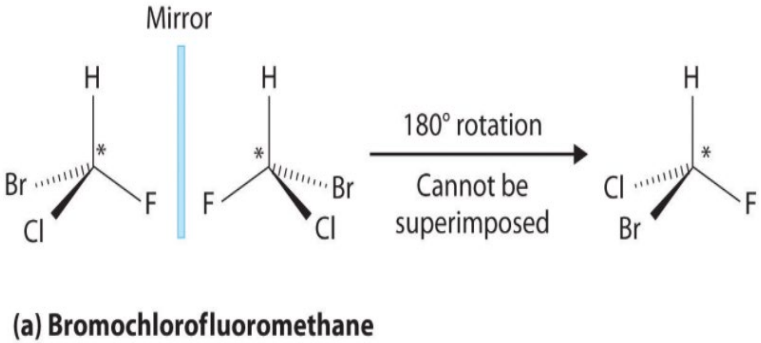
(B) 

(C) 

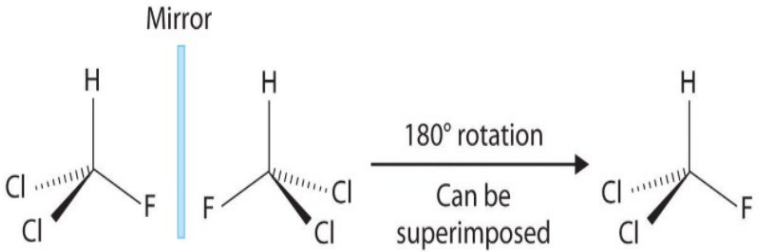
(D) 

Chirality

- Def: A molecule whose mirror image can not be superimposed. Typically these molecules are optically active.
- A racemic mixture is a 50/50 mix of the D & L formations causing to appear not optically active.



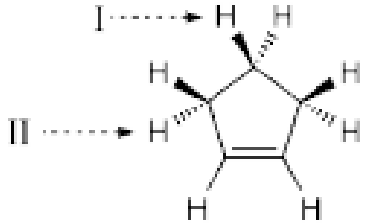
(a) Bromochlorofluoromethane



(b) Dichlorofluoromethane

2020 National Exam

55. Replacing which hydrogens with chlorine would give a chiral molecule?



(A) I only

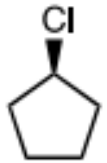
(B) II only

(C) Either I or II

(D) Neither I nor II

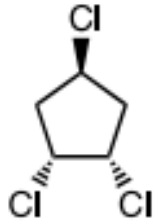
2017 National Exam

55. Which of the following molecules is chiral?

(A) 

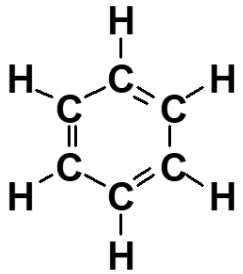
(B) 

(C) 

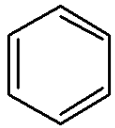
(D) 

Aromatics:
Benzene and Benzene Derivatives

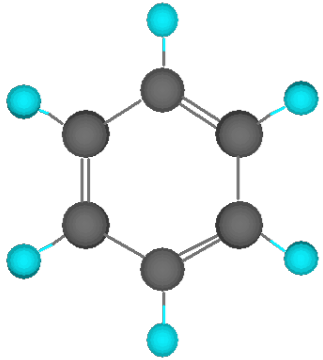
- Aromatic compound: a hydrocarbon that contains one or more benzene-like rings. Formula: C_6H_6
- The double/single bonds have resonance.
  - Arene: a term used to describe aromatic compounds.
  - Kekulé structure for benzene (1872).



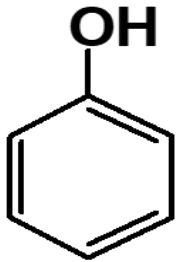
A Kekulé structure showing all atoms



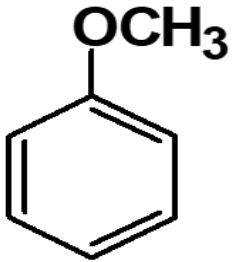
A Kekulé structure as a line-angle formula



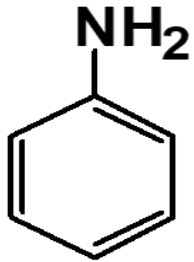
Common Monosubstituted Benzenes and Polynuclear Aromatic Hydrocarbons (PAHs):



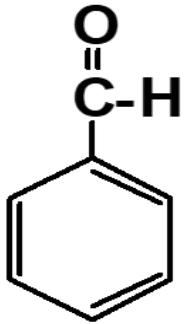
Phenol



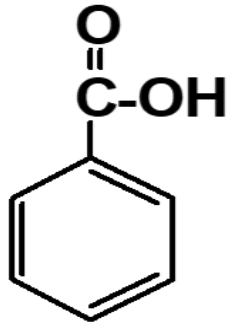
Anisole



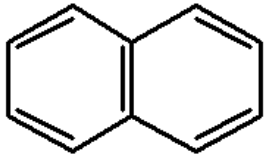
Aniline



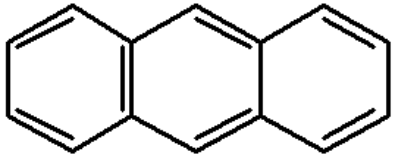
Benzaldehyde



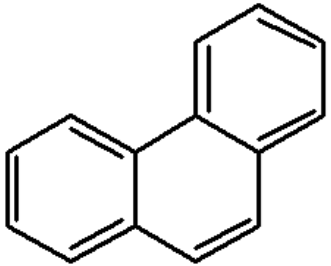
Benzoic acid



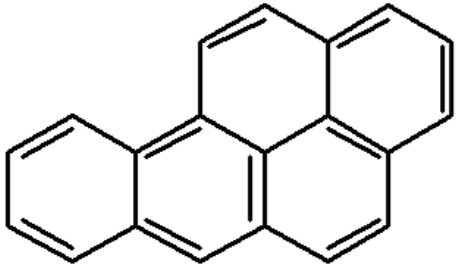
Naphthalene



Anthracene



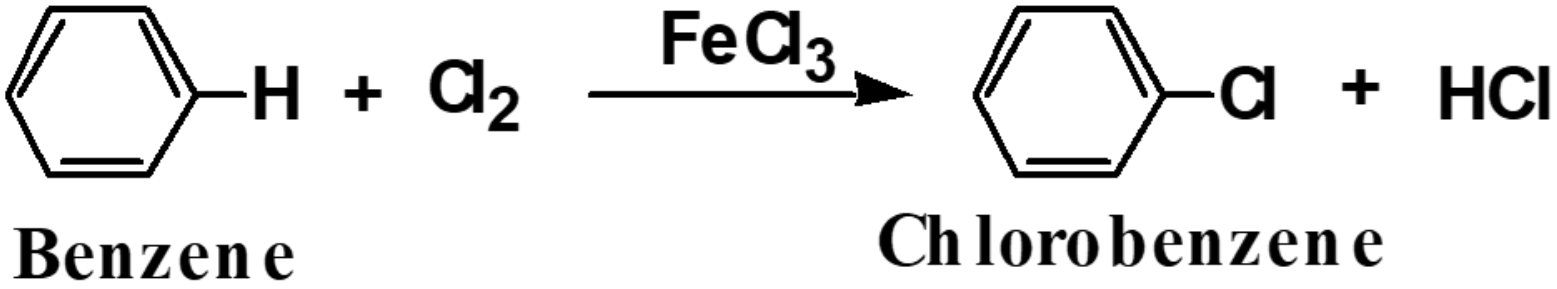
Phenanthrene



Benzo[a]pyrene

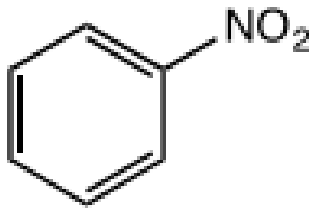
Aromatic Substitution: Most characteristic reaction of an aromatic compound.

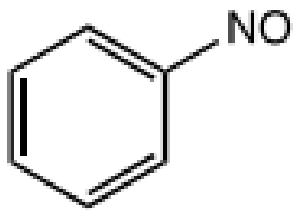
- Some groups that can be directly introduced directly on the ring are the halogens, the nitro ($-NO_2$) group, and the sulfonic acid ($-SO_3H$) group.
- Halogenation:

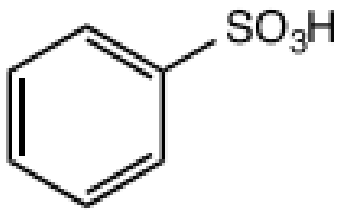


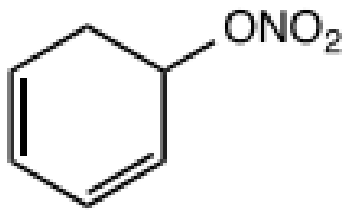
2016 National Exam

58. What is the product of the reaction of benzene with a solution of nitric acid in sulfuric acid at 50 °C?

(A) 

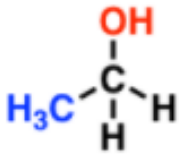
(B) 

(C) 

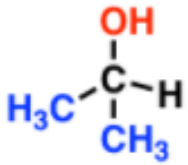
(D) 

Alcohols

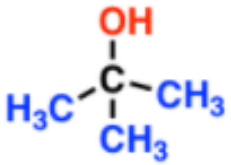
- Alcohols are classified by how many carbon are attached to the carbon that is attached to the hydroxyl.
- If there are more than one hydroxyl group attached numeric prefixes are added before the -ol. The additional hydroxyl groups increase the boiling point of the molecule.



Primary alcohol



Secondary Alcohol



Tertiary Alcohol

Common Reactions of Alcohols

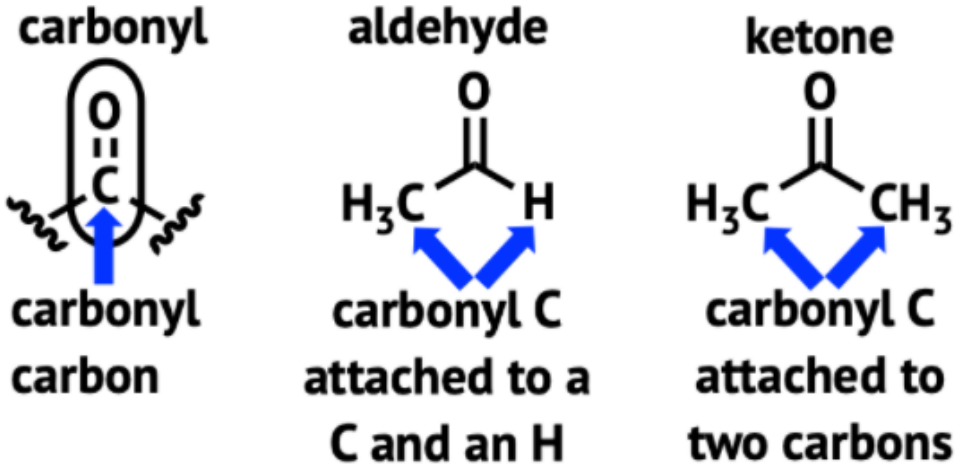
- Acid-Catalyzed Dehydration: alcohol → alkene* + water

** follows Zaitsev's Rule - the double bond will form on the most highly substituted carbon. The trans formation is more stable than the cis.*

- Oxidation
  - 1° alcohol → aldehyde → carboxylic acid
  - 2° alcohol → ketone
  - 3° alcohol resists oxidation
- Substitution forming alkyl halides: alcohol + acid halide → alkyl halide and water
- Fischer Esterfication: alcohol + carboxylic acid → ester

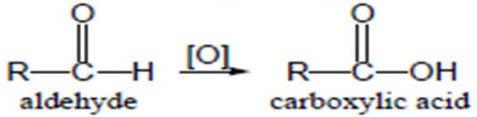
Aldehydes and Ketones

- Both aldehydes and ketones contain carbonyls, it is the location of the carbonyl that differentiates the two. For an aldehyde the carbonyl is located on a terminal carbon, and for a ketone the carbonyl must be on an interior carbon.

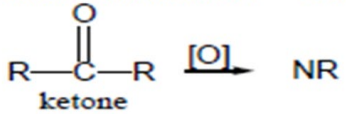


Common Reactions
Aldehydes and Ketones

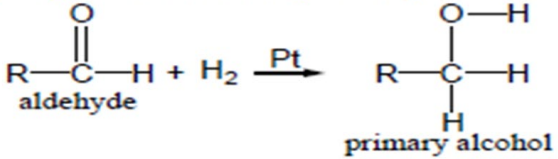
1. **Oxidation of Aldehydes to give Carboxylic Acids**



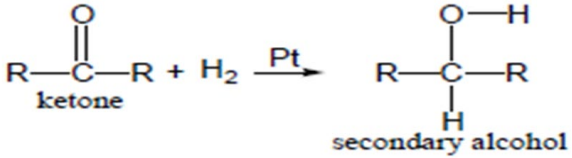
2. **Oxidation of Ketones — No Reaction**



3. **Hydrogenation of Aldehydes to give Primary Alcohols**

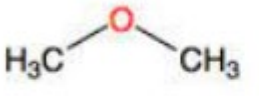


4. **Hydrogenation of Ketones to give Secondary Alcohols**

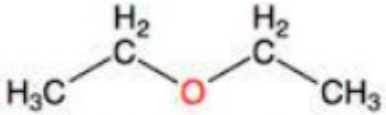


Ethers

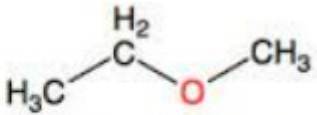
- Organic compounds that contain an oxygen bonded to two carbon groups. Highly unreactive, these compounds are excellent solvents for organic reactions.
- Produced by the Williamson Ether Synthesis reaction



dimethyl ether
(Methoxymethane)

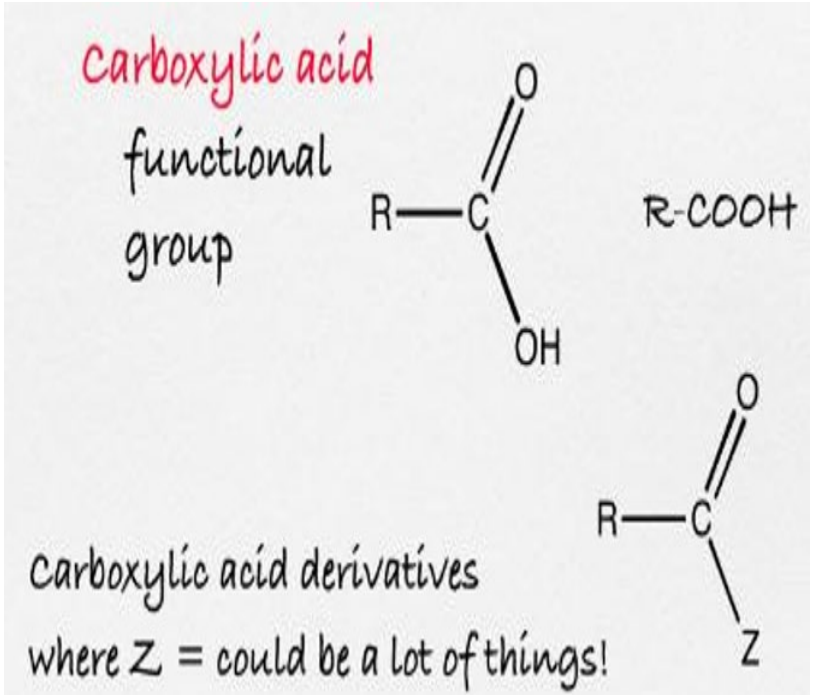


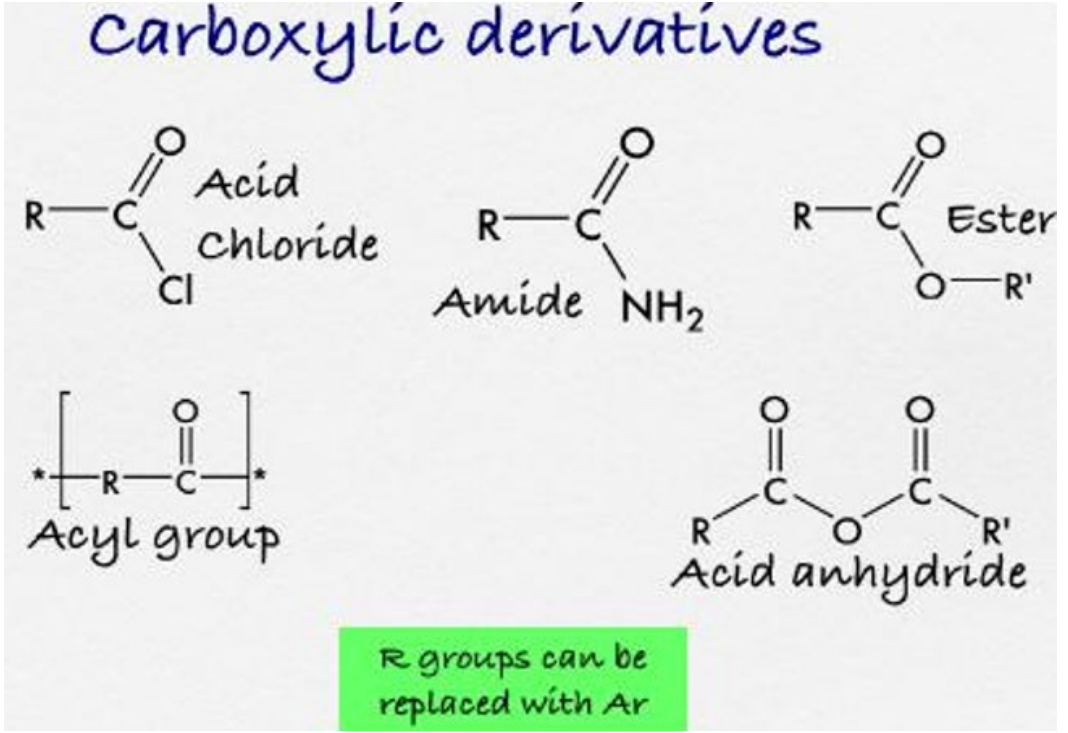
diethyl ether
(Ethoxyethane)



ethyl methyl ether
(Methoxyethane)

Carboxylic Acids and Acid Derivatives





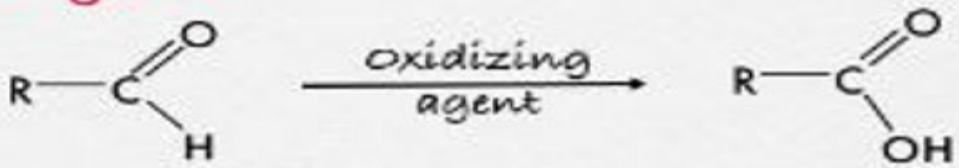
Common Carboxylic Acids

Common	IUPAC	Formula
Formic	methanoic	$HCOOH$
Acetic	ethanoic	CH_3COOH
Butyric	butanoic	$CH_3(CH_2)_2COOH$
Capric	decanoic	$CH_3(CH_2)_8COOH$
Lauric	dodecanoic	$CH_3(CH_2)_{10}COOH$
Steric	octadecanoic	$CH_3(CH_2)_{16}COOH$

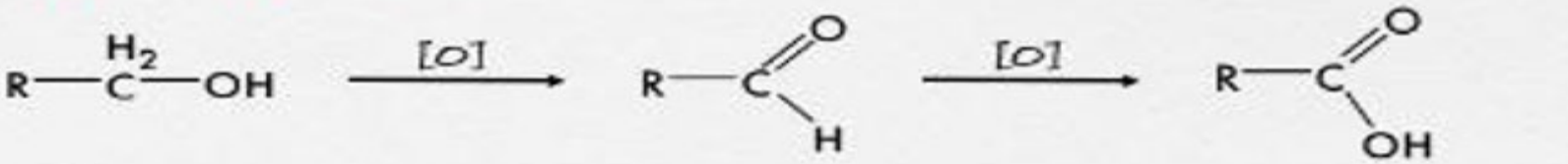
Formation of a Carboxylic Acid

Produced by oxidation of

aldehydes

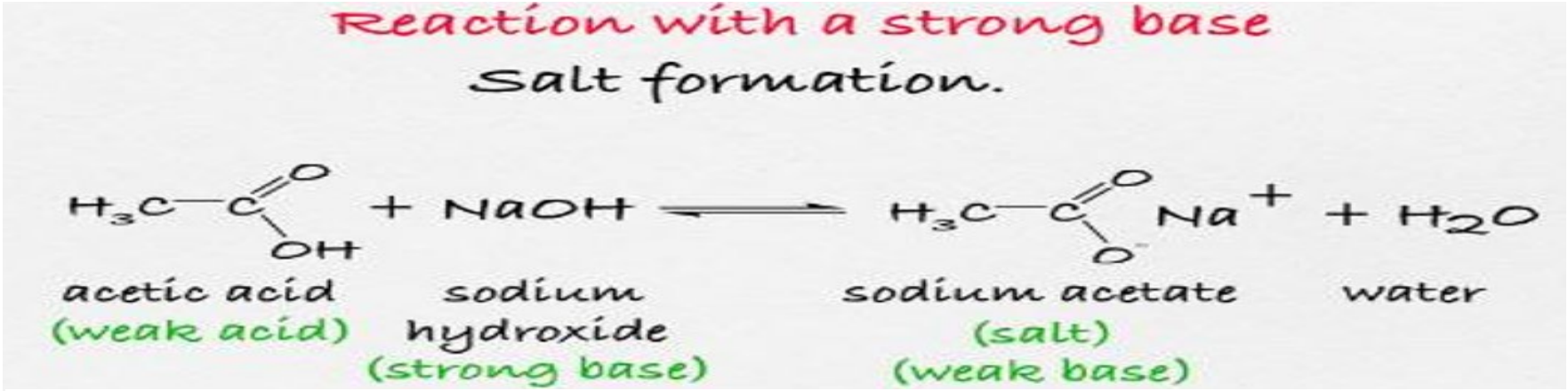


primary alcohols

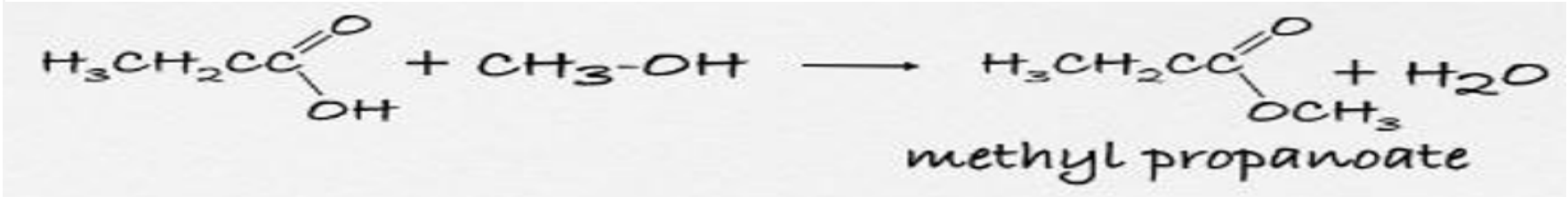


1° alcohol aldehyde carboxylic acid

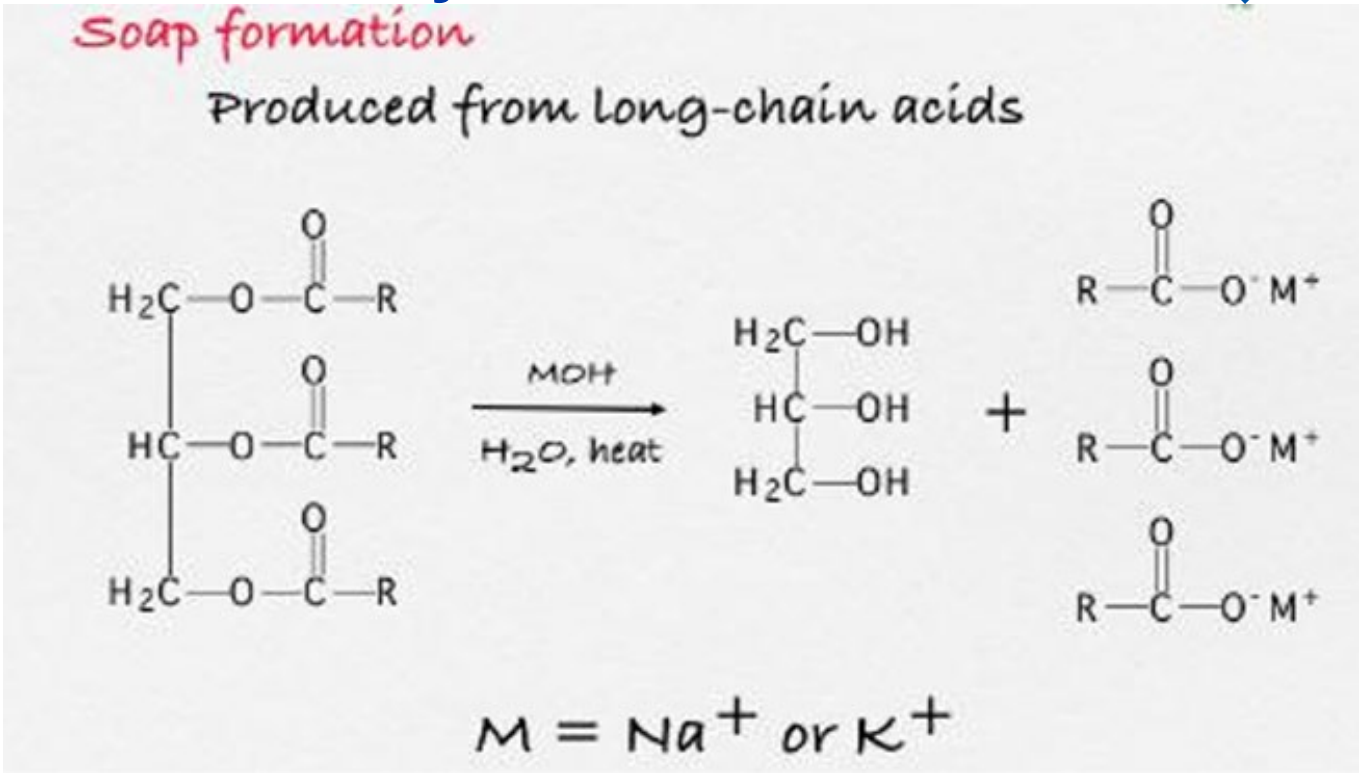
Common Carboxylic Acid Reactions



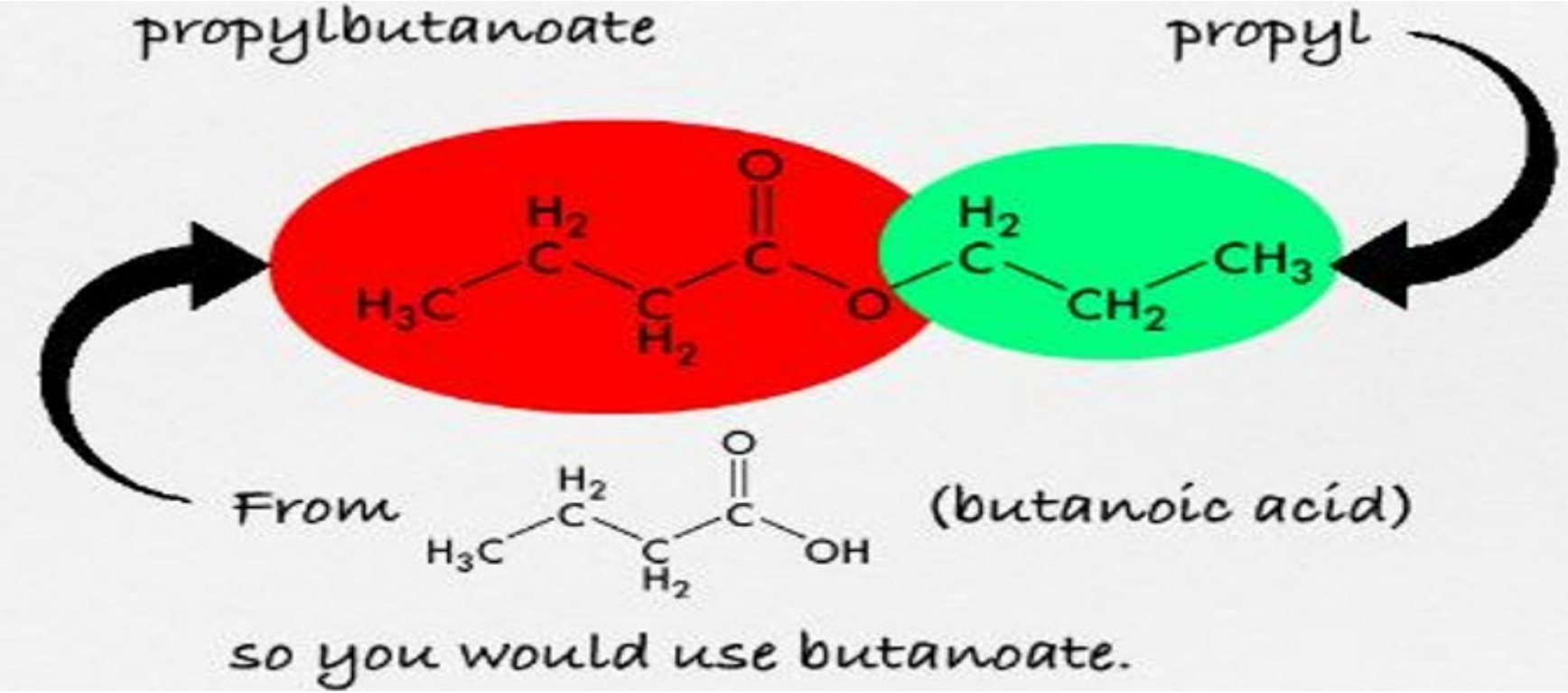
Esterfication



Common Carboxylic Acid Reactions

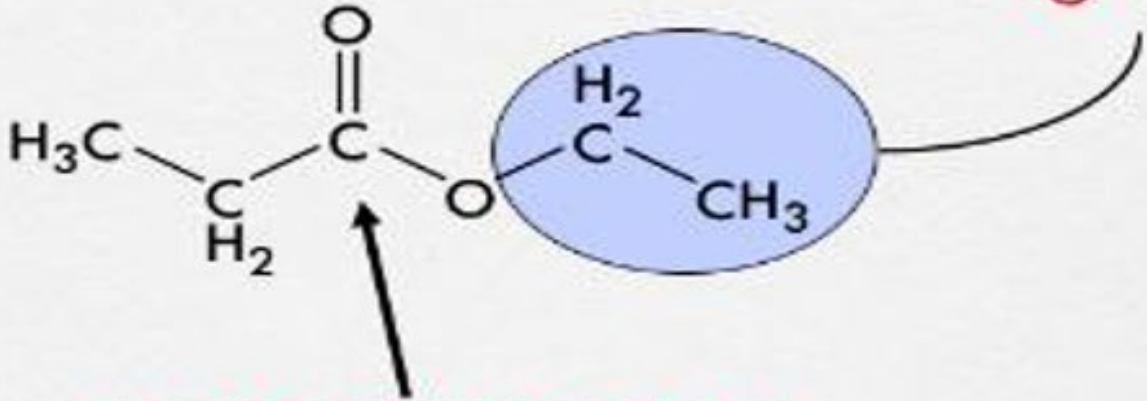


Esters


propylbutanoate
propyl
From
(butanoic acid)
so you would use butanoate.

Esters

This part is treated like a branch with a -yl ending.



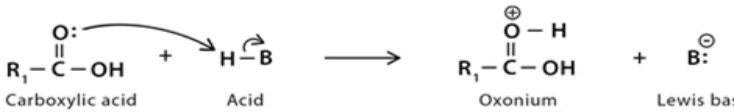
Look for this carbon

It is the number one carbon on the original acid - it is given the -oate ending.

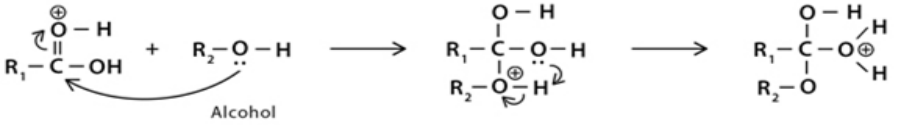
Mechanism of Fischer Esterification

ACS Chemistry for Life®

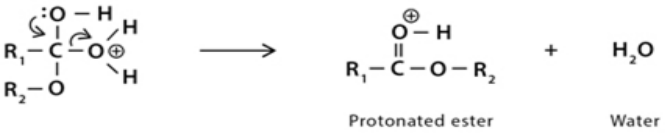
Step 1: Protonation of the carbonyl group of the carboxylic acid by the catalyst



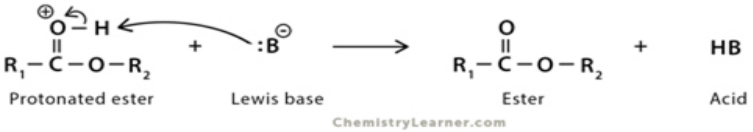
Step 2: Nucleophilic attack on the carbonyl by the alcohol and subsequent cleavage of the pi bond results in an oxonium ion which then rearranges itself after proton transfer



Step 3: Elimination of water followed by a pi bond formation between C and O results in a protonated ester



Step 4: Deprotonation of the protonated ester by the Lewis base gives the desired ester



2021 Local Section Exam

58. Which combination of reactants and catalyst will produce methyl propanoate, $CH_3CH_2COOCH_3$, upon heating?

(A) CH_3CH_2OH and CH_3COOH with catalytic NaOH

(B) CH_3CH_2OH and CH_3COOH with catalytic H_2SO_4

(C) CH_3OH and CH_3CH_2COOH with catalytic NaOH

(D) CH_3OH and CH_3CH_2COOH with catalytic H_2SO_4

2021 National Exam

55. Which of these could have the formula $C_6H_{12}O$?

I. An acyclic ester
II. A cyclic ether

(A) I only
(B) II only
(C) Either I or II
(D) Neither I nor II

2016 National Exam

55. A student wishes to prepare ethyl acetate from the reaction of ethanol and acetic acid. To be successful, this reaction requires

(A) an acidic catalyst.

(B) a basic catalyst.

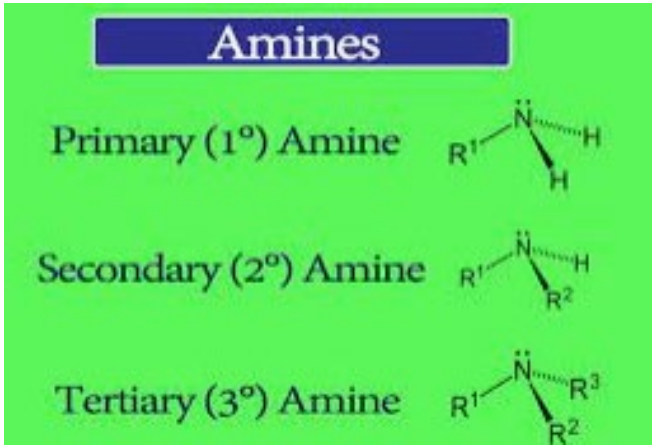
(C) an oxidizing agent.

(D) a reducing agent.

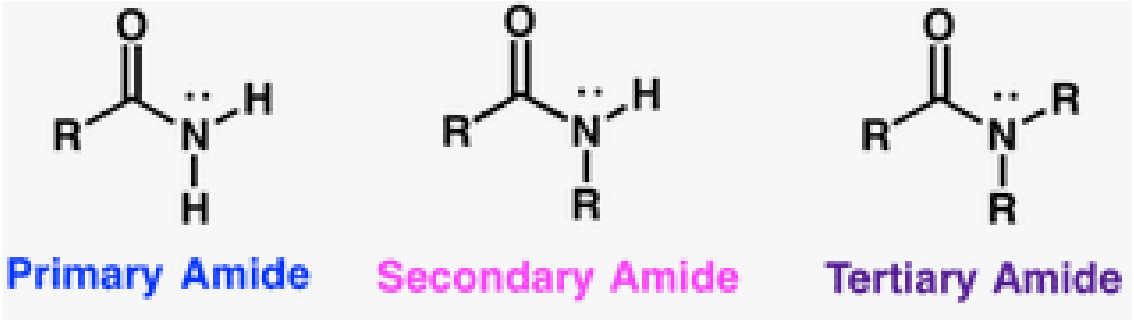
Amines and Amides

- Classification of amines:

** side note amines stink -- they really smell bad!*



- Classification of amides:



Amine vs. Amide

Composed of C, H, N atoms	Composed of C, H, N, O
Does not contain a carbonyl	Contains a carbonyl
Show basicity	Show acid characteristics
Most low molecular weight amines are gases at room temperature or are easily vaporized	Most amides are solids at room temperature
Have relatively lower boiling points	Have relatively higher boiling points
Dyes, polymers, vitamins and medications	Found in amino acids and proteins

2021 Local Section Exam

57. An amine with the formula $C_4H_{11}N$ will have which of these properties?

(A) Unpleasant odor

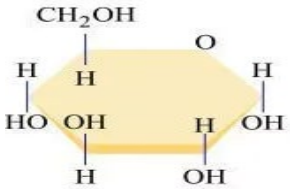
(B) Boiling point greater than 100 °C

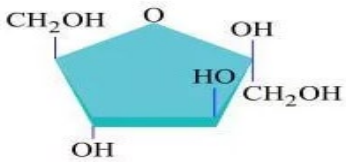
(C) Absorption of light with $\lambda > 450$ nm

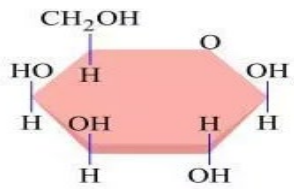
(D) Water solubility less than 10 g/L

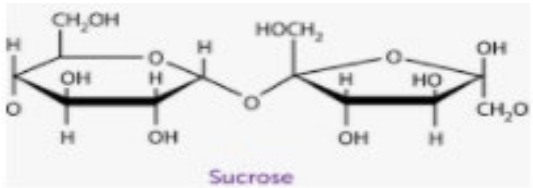
Carbohydrates

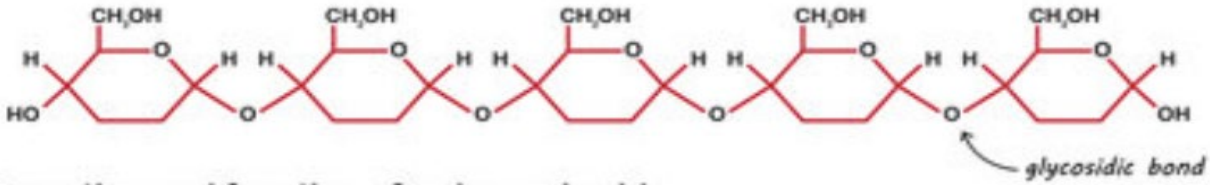
- Carbohydrates are polymers made from monomers called monosaccharides.
- Monosaccharides link together to form disaccharides.
- Chains of monosaccharides are referred to as polysaccharides or carbohydrates.





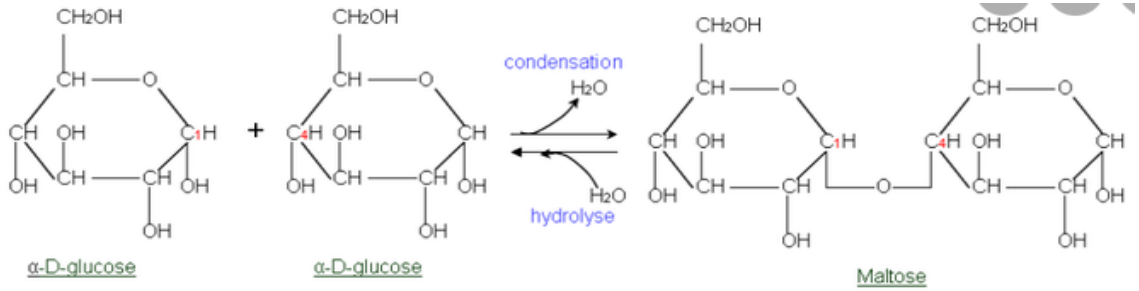


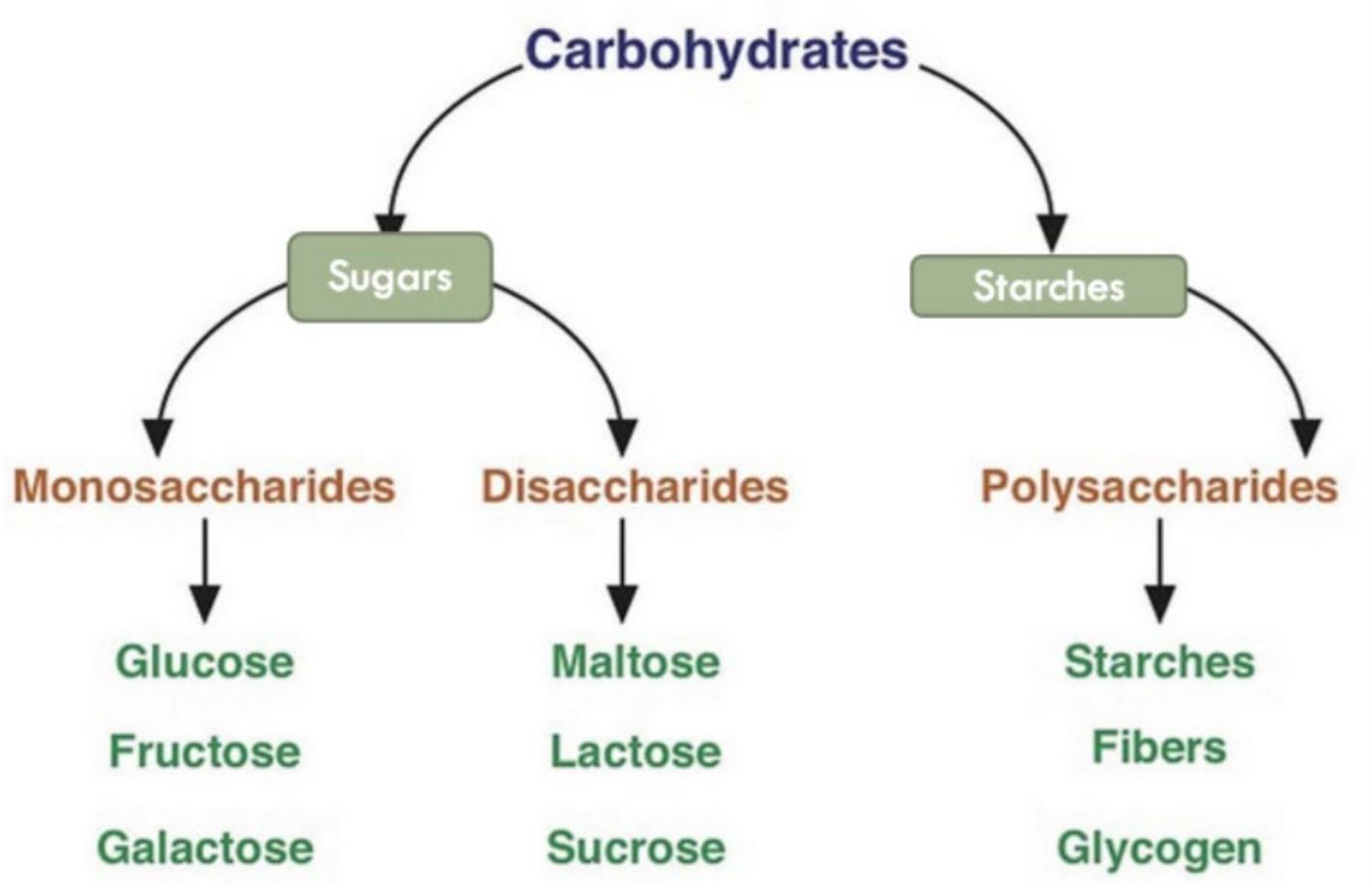




Monosaccharides

- Simple sugars that cannot be hydrolyzed into simpler molecules. They can be categorized based on their structure as polyhydroxyaldehydes (aldoses) or polyhydroxyketones (ketoses).
- Monosaccharides can be joined together through a **dehydration synthesis** that creates a **glycosidic bond.** Monosaccharides can be formed by the **hydrolysis** of a polysaccharide.



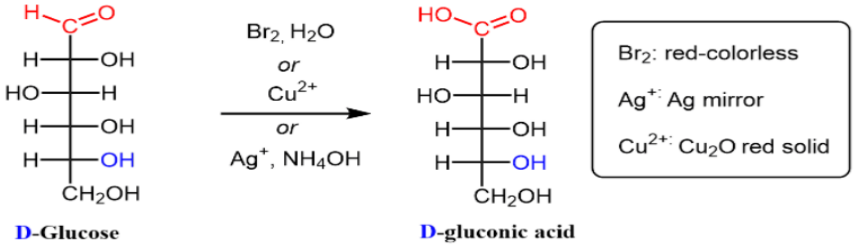

Carbohydrates
Sugars
Starches
Monosaccharides
Disaccharides
Polysaccharides
Glucose
Fructose
Galactose
Maltose
Lactose
Sucrose
Starches
Fibers
Glycogen

Common Reactions of Carbohydrates

- Reduction: Sugar → sugar alcohol
- Oxidation: Aldehyde or alcohol → carboxylic acid
- Dehydration Synthesis: Monosaccharides → polysaccharides
- Hydrolysis: Polysaccharides → monosaccharides
- Hemiacetal Formation: aldehyde + alcohol → hemiacetal
- Fermentation: sugar + enzymes → alcohol + carbon dioxide

Carbohydrate Reactions

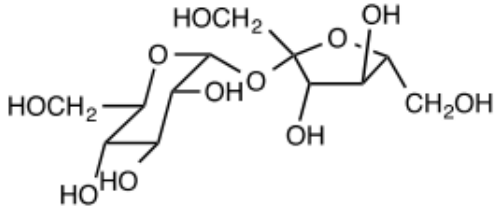
- Strong Oxidizers to know:
  - Tollen's Reagent (silver mirror test)
  - Fehling's Reagent (produces a red copper precipitate
  - Benedict's Reagent (produces a red copper precipitate - often used in glucose concentration reactions)
  - Bromine water (changes from red to colorless)



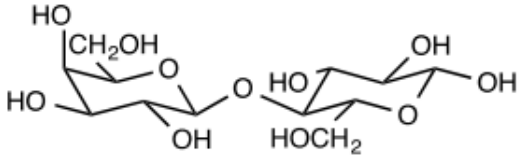
2016 National Exam

60. Tollens' reagent, basic diamminesilver(I) solution, gives a positive test (in the form of a silver mirror) in the presence of aldehydes. Which sugars give a positive Tollens' test?

I. Sucrose,



II. Lactose,

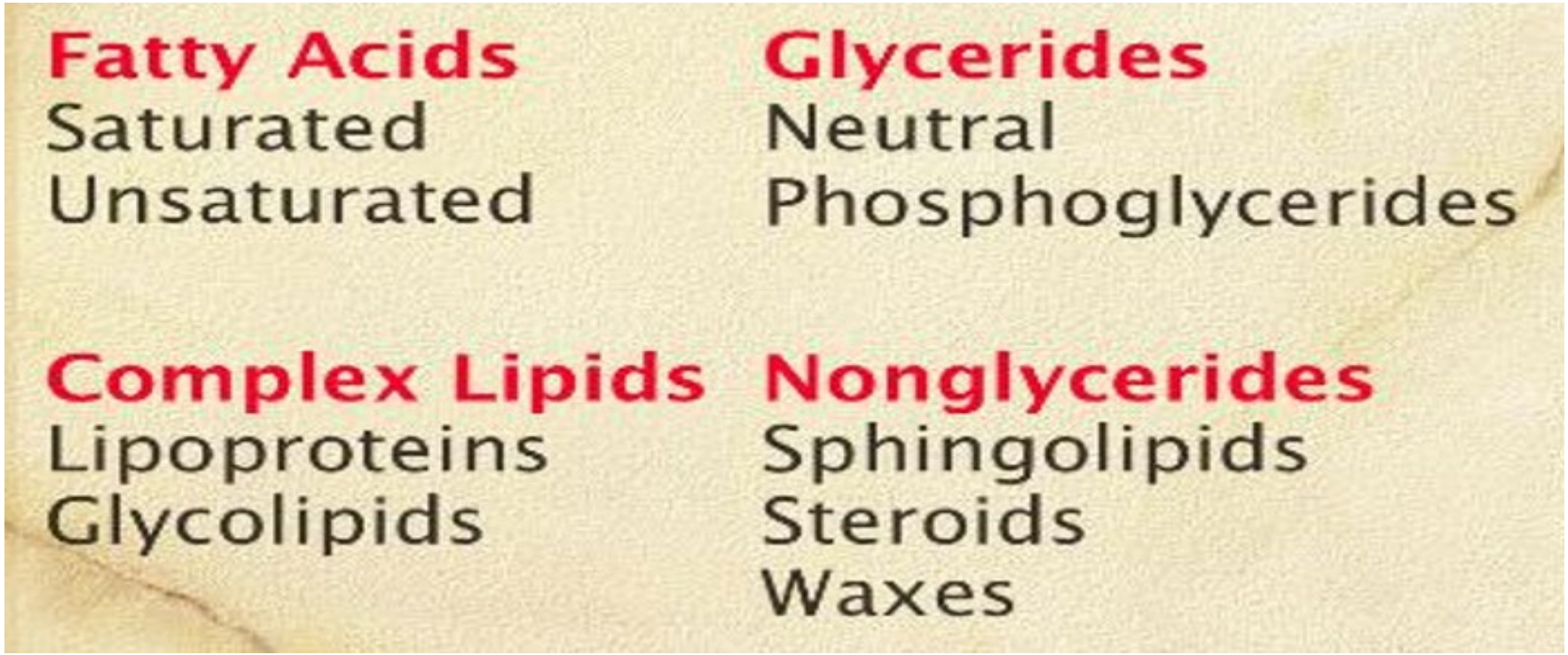


(A) I only **(B)** II only

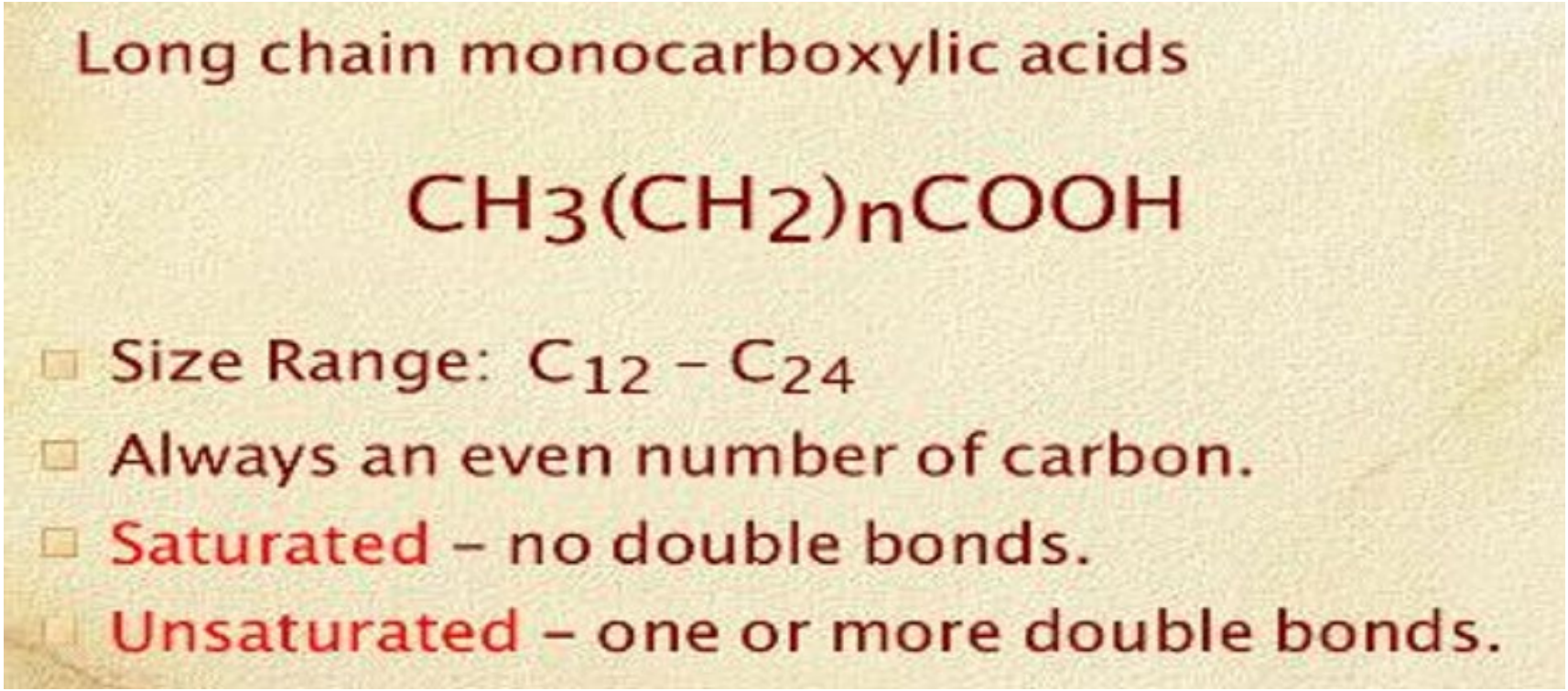
(C) Both I and II **(D)** Neither I nor II

www.acs.org/Olympiad

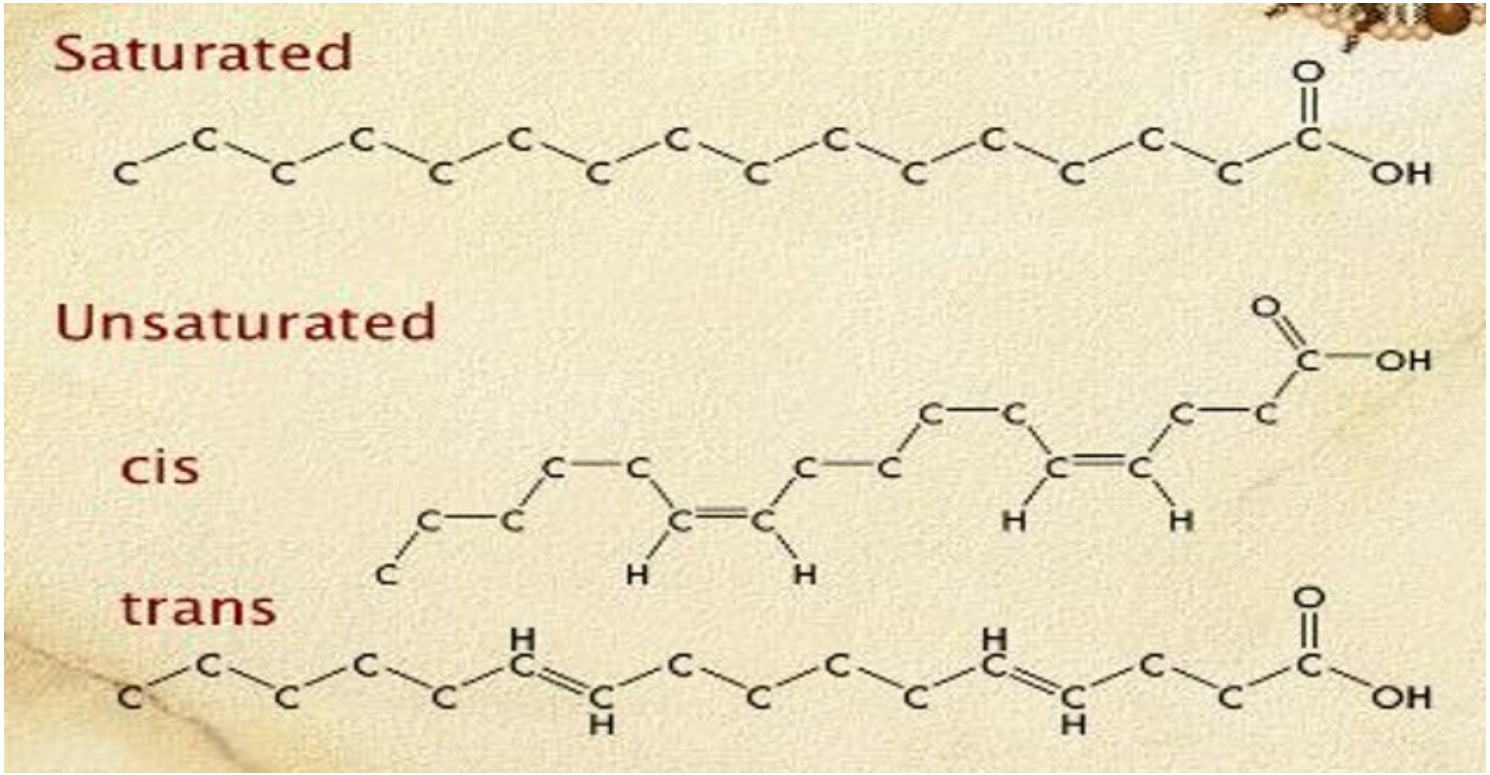
Lipids


Fatty Acids
Saturated
Unsaturated
Glycerides
Neutral
Phosphoglycerides
Complex Lipids
Lipoproteins
Glycolipids
Nonglycerides
Sphingolipids
Steroids
Waxes

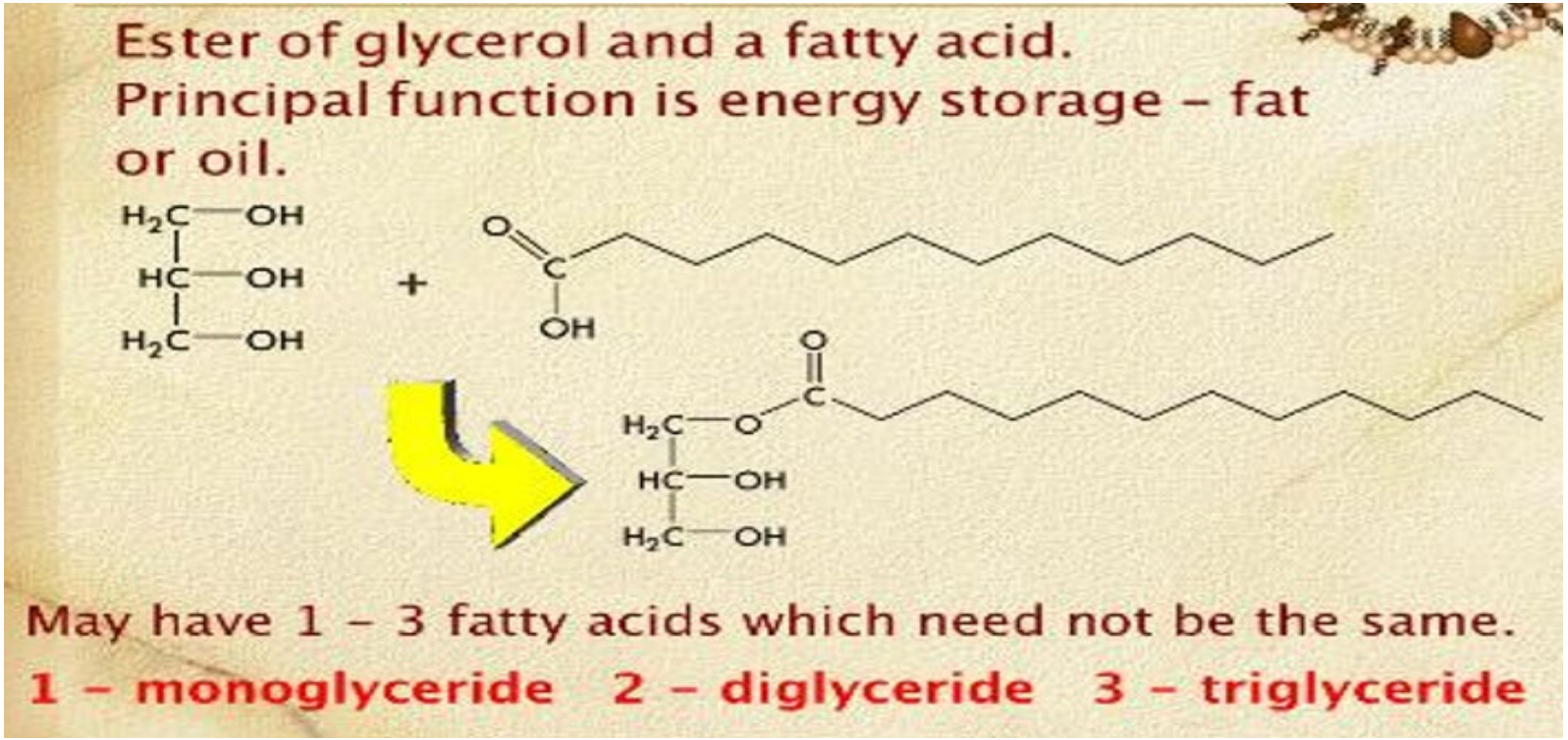
Lipids


Long chain monocarboxylic acids
$CH_3(CH_2)_nCOOH$
Size Range: $C_{12} - C_{24}$
Always an even number of carbon.
Saturated – no double bonds.
Unsaturated – one or more double bonds.

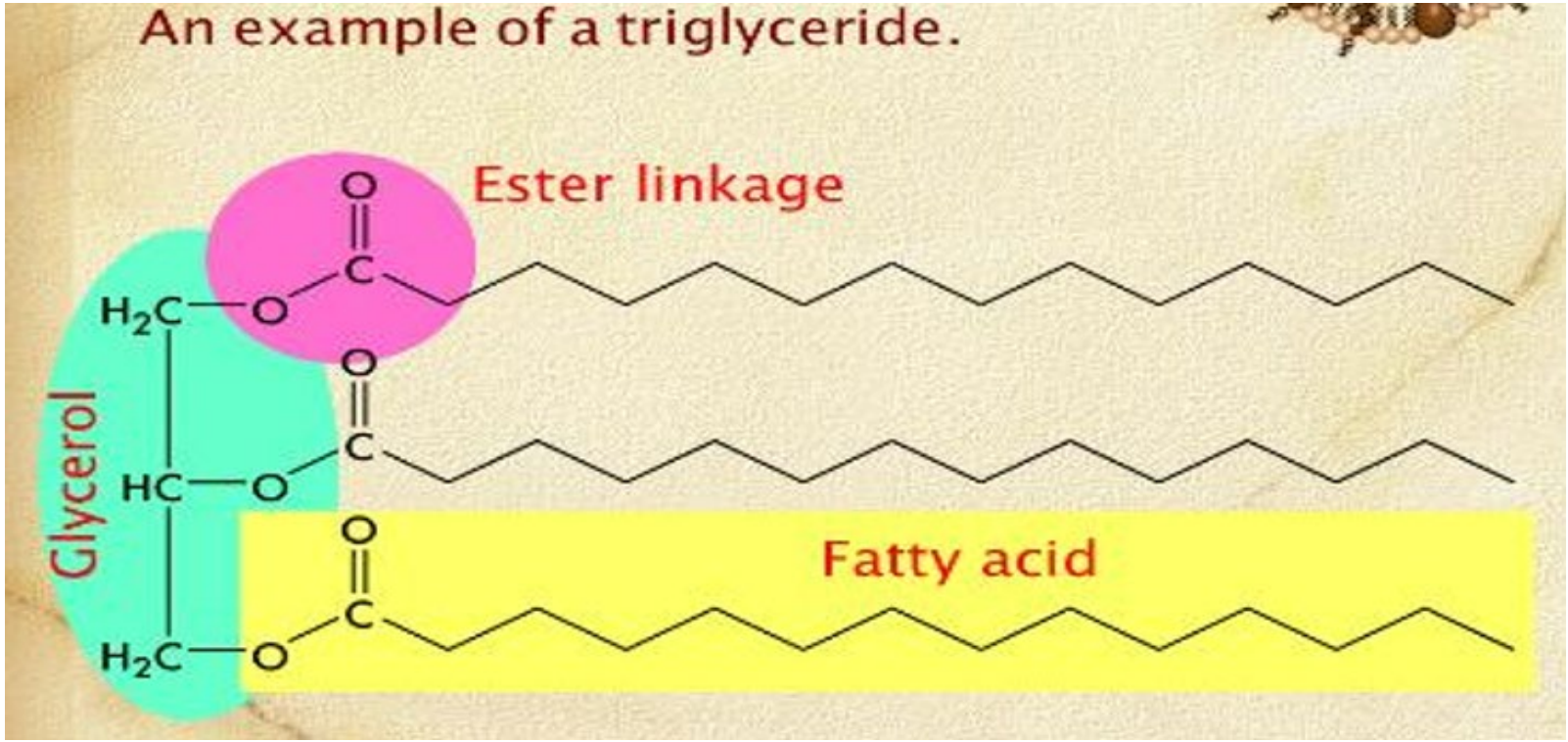
Lipid Structure



Lipid Structure

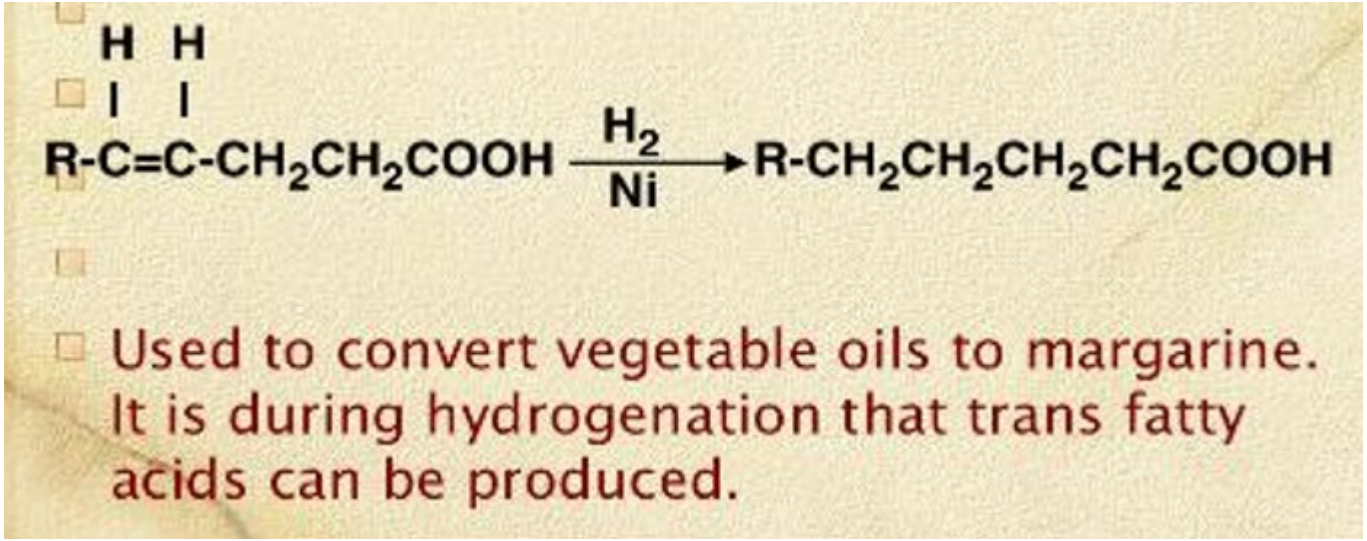


Lipid Structure: Triglyceride



Common Reactions of Fatty Acids and Lipids

- Fatty acid reactions are like the reactions of any other carboxylic acid. Unsaturated fatty acids can undergo hydrogenation so that the double bonds are eliminated.

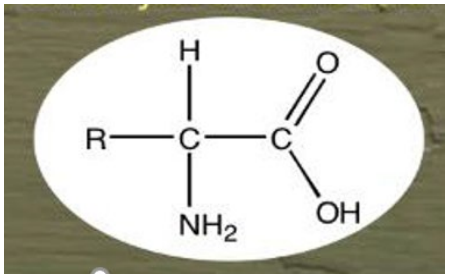


Amino Acids and Proteins

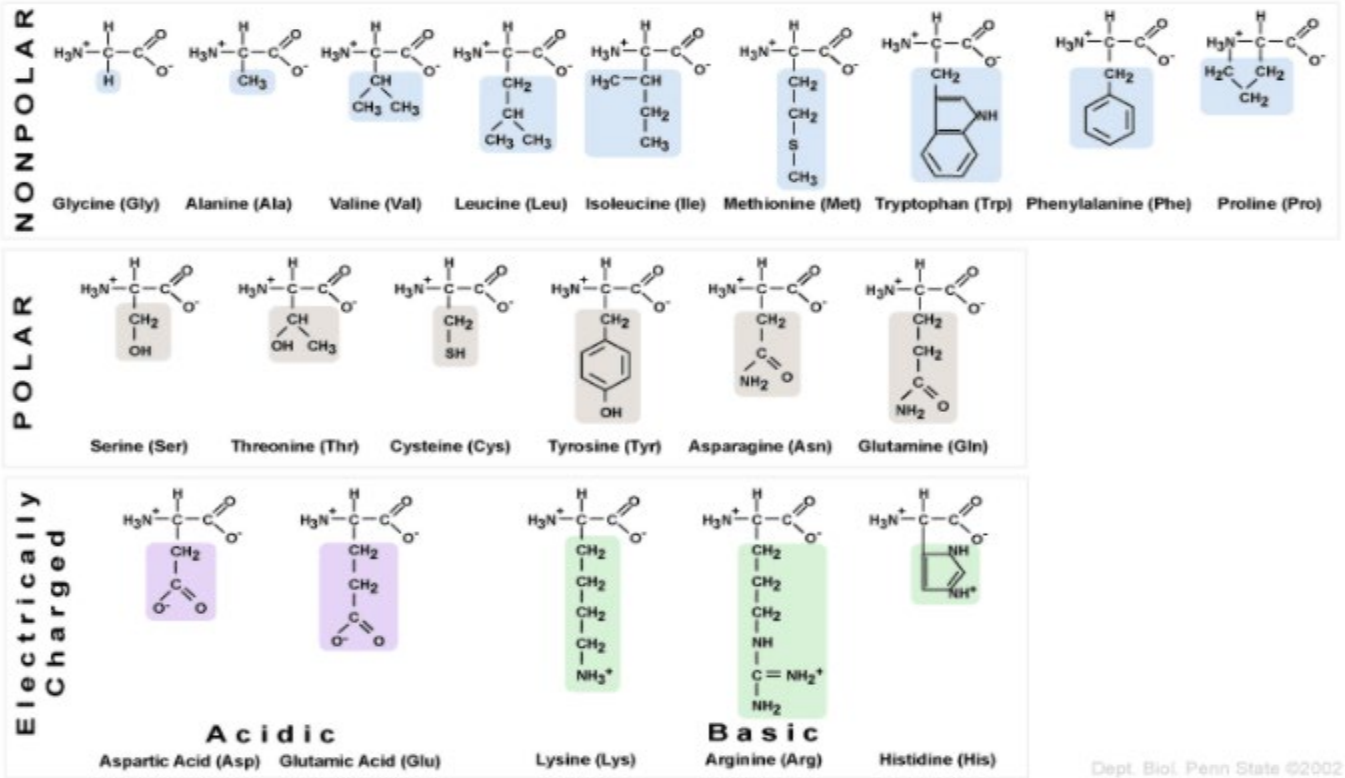
- There are 20 common amino acids. Amino acids have a common structure. It is the “R” or side chain that differentiates the amino acids.
- Amino Acids are joined together through a dehydration synthesis reaction that forms peptide bonds and chains of amino acids.
- These chains of amino acids are polymers called peptides and proteins.
- The number of possible combinations for a polypeptide chain can be determined if given the number of amino acids available and the length of the chain by raising the number of amino acids to the power of the length of the chain.

60. How many possible dipeptides can be formed using the twenty commonly occurring amino acids?

(A) 40 **(B)** 200 **(C)** 210 **(D)** 400



Classifying Amino Acids Based on R group



2017 National Exam

59. The isoelectric point of a protein is the pH at which it is electrically neutral. Which mutation of an amino acid $NH_2CHRCOOH$ in the protein would have the greatest effect on its isoelectric point, assuming that the mutation does not significantly affect the protein's overall structure?

(A) Serine ($R = CH_2OH$) $\rightarrow$ Lysine ($R = CH_2CH_2CH_2CH_2NH_2$)

(B) Glutamine ($R = CH_2CH_2CONH_2$) $\rightarrow$ Methionine ($R = CH_2CH_2SCH_3$)

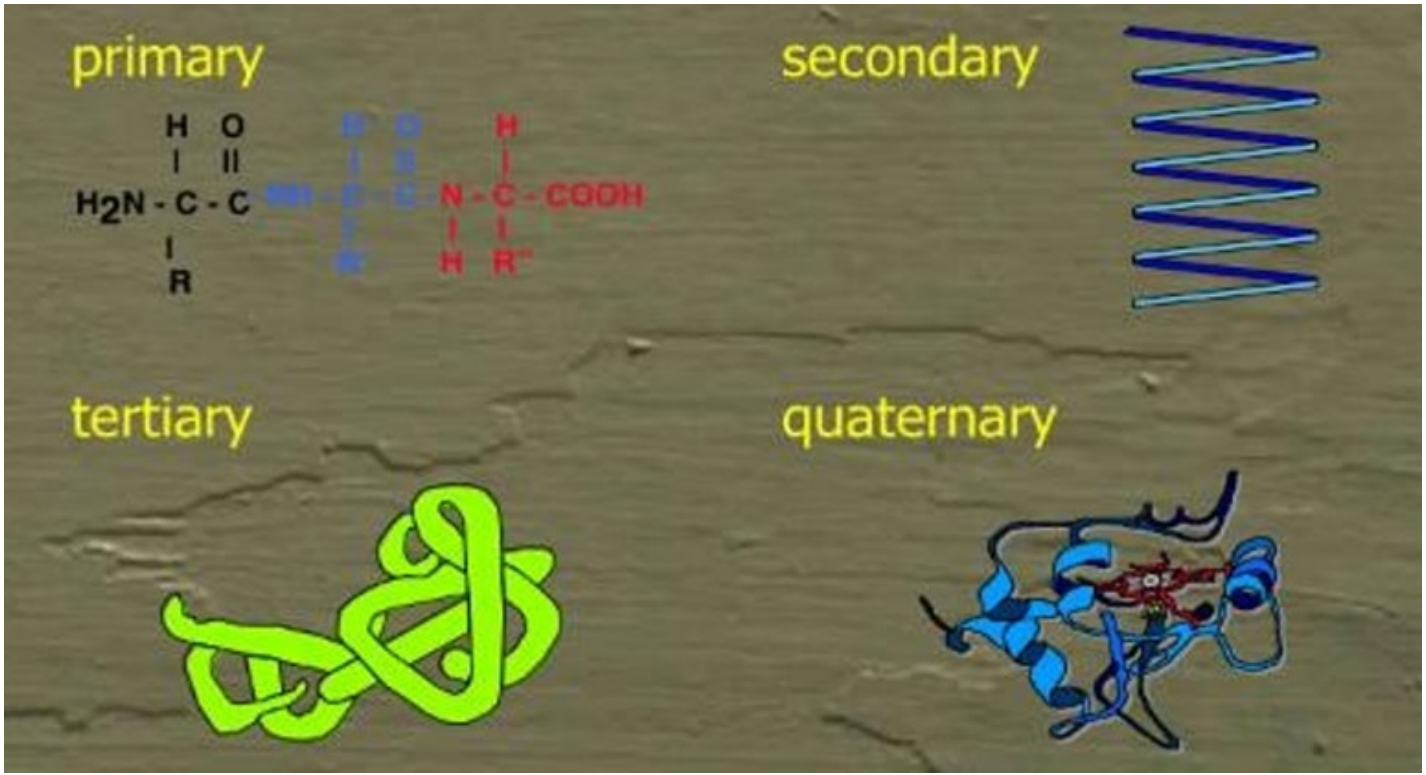
(C) Isoleucine ($R = CH[CH_3]CH_2CH_3$) $\rightarrow$ Valine ($R = CH[CH_3]_2$)

(D) Alanine ($R = CH_3$) $\rightarrow$ Glycine ($R = H$)

Structure of a Protein

- 1° structure is the linear arrangement of the amino acid sequence
- 2° structure refers to the repeated folding or curling pattern - this structure is dependent on Hydrogen bonding
- 3° structure is a result of additional folding based on attraction and repulsion of the side chains (R-groups) on the amino acids
- 4° structures are formed when several smaller proteins interact to form one larger protein

Summary of Protein Structure



Denaturing of a Protein

- Heat – ↑ in temp, ↑ vibrations within the molecule, the energy of these vibrations can disrupt the 3°
- pH – ↑ or ↓ pH, affect the charges of protein, the electrostatic interactions that normally stabilize the native conformation is reduced.
- Detergents (eg. SDS) - disrupt hydrophobic interactions, if the detergent is charged, this can also disrupt electrostatic interactions
- Reducing agents(eg. Urea) – will form stronger H bonds, stronger than within the protein. Also disrupt the hydrophobic interaction
- Heavy metal ions
- Mechanical stress

2016 National Exam

59. An enzyme catalyzes the hydrolysis of an ester with a certain activity, but this activity is lost in a 3 M urea solution. What is the most likely explanation for the loss of activity?

(A) Urea binds to the active site of the enzyme competitively with the substrate.

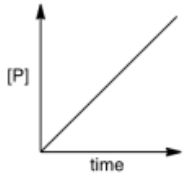
(B) Urea causes the cleavage of the peptide bonds in the enzyme.

(C) Urea causes the enzyme to denature and lose its specific three-dimensional shape.

(D) Urea reacts with disulfide bonds in the enzyme.

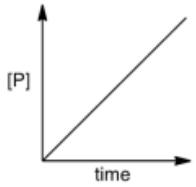
2018 National Exam

60. An enzyme catalyzes the transformation of a substrate into a product P, with the appearance of product over time as shown below:

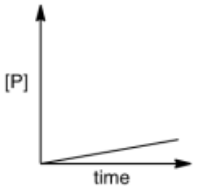


Under the same conditions, except in the presence of a competitive inhibitor of the enzyme, which graph best represents the appearance of product over time?

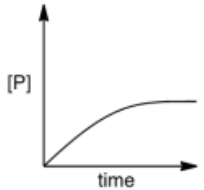
(A)



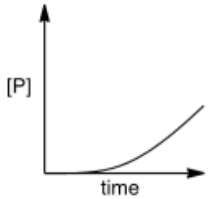
(B)



(C)

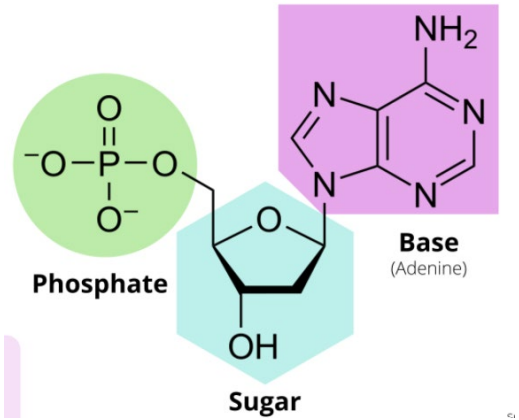


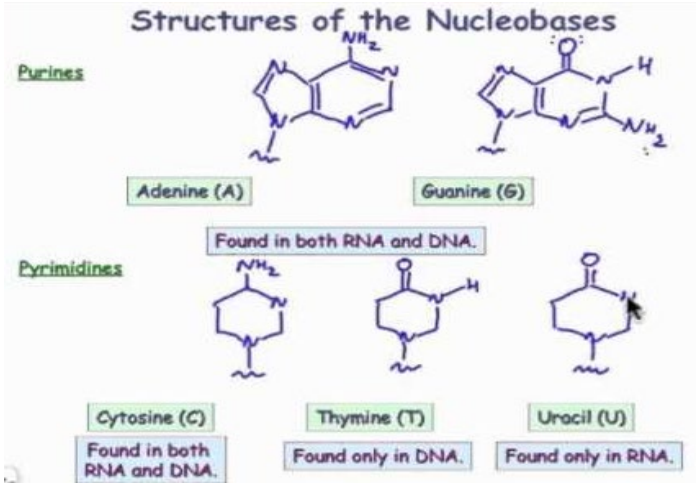
(D)



Nucleic Acids

- Nulceic Acids, Deoxyribonucleic Acid (DNA) and Ribonucleic Acid (RNA), are made from smaller units called nucleotides. Each of these nucleotides have a phosphate group, a 5 carbon sugar and a nitrogen base.

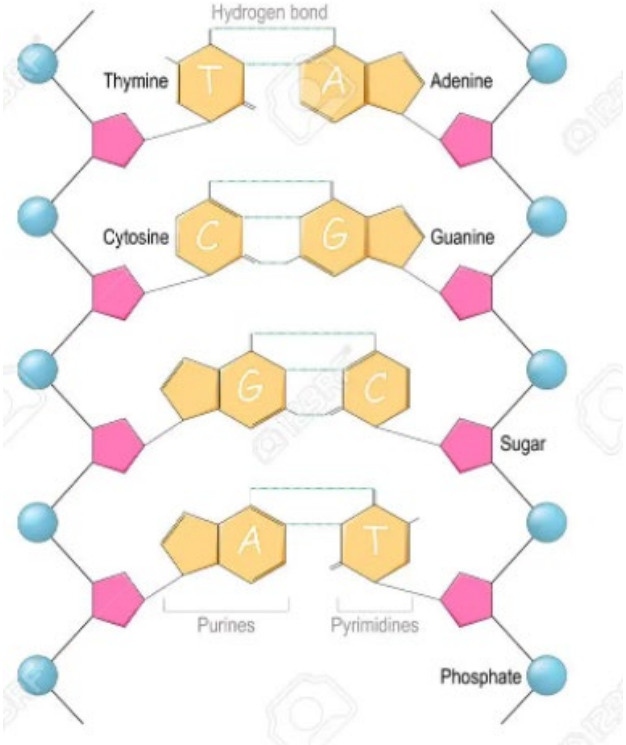




Nucleic Acids

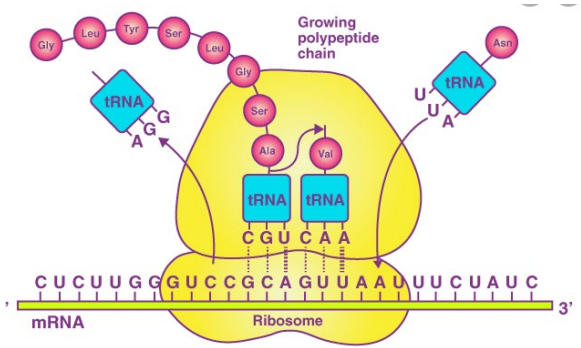
DNA is double stranded, the two strands are brought together by the hydrogen bonds that form between the nucleobases. Two hydrogen bonds will form between A=T, and three will form between AΞG.

DNA is found within the nucleus. New DNA is made through replication and new RNA is made through transcription.

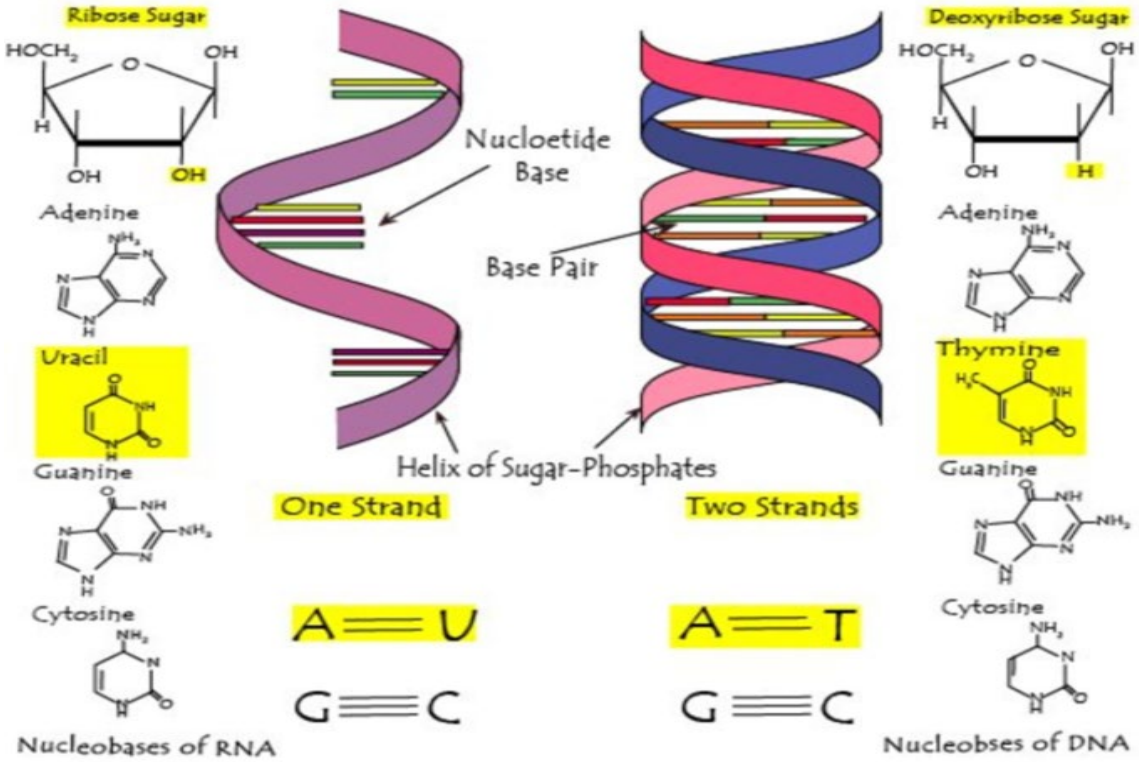


Nucleic Acids

- RNA is single stranded, and there are many types of RNA each dictated by the job of the RNA.
  - mRNA messenger RNA carries the genetic information from the nucleus to the ribosomes for protein synthesis
  - tRNA transfer RNA brings the amino acids to the ribosome for translation
  - rRNA ribosomal RNA create the ribosomes



RNA vs. DNA


Ribose Sugar
HOCH2
O
OH
H
OH
OH
Adenine
Uracil
Guanine
Cytosine
Nucleobases of RNA
Nucleotide Base
Base Pair
Helix of Sugar-Phosphates
One Strand
Two Strands
A = U
G ≡ C
A = T
G ≡ C
Deoxyribose Sugar
HOCH2
O
OH
H
OH
H
Adenine
Thymine
Guanine
Cytosine
Nucleobses of DNA

2021 Local Section Exam

60. Which element is NOT present in DNA?

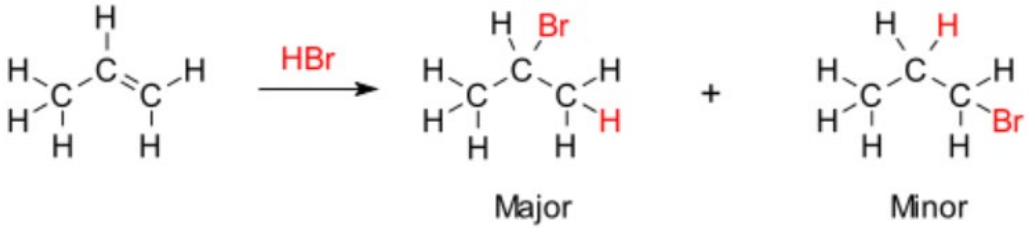
(A) H **(B)** N **(C)** P **(D)** S

Important Terms

- Electrophiles: electron poor reagents, they seek electrons.
- Nucleophiles: electron rich reagents, they donate electrons.
- Carbocation: a carbon atom that has had its electrons pulled away by an electrophile and now has a positive charge.
- Leaving group: the product that completes the reaction generally as an anion.

Carbocation

- **Carbocations** can be categorized as primary, secondary or tertiary according to how many organic attachments it has.
- Tertiary carbocations are most stable, where primary are most reactive.
- **Markovnikov's rule** restated: the electrophilic addition will occur in such a way to involve the most stable carbocation. For example In the addition of HX to an unsymmetrical alkene, the hydrogen will attach to the carbon that has the higher number of hydrogen already present.



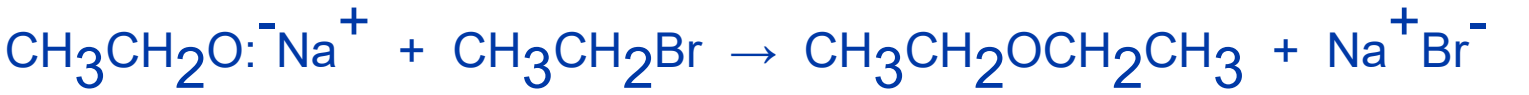
Nucleophilic Substitution Reaction

- Nucleophile + substrate → product + leaving group
- This means that when one bond is broken a new and different bond is formed. The leaving group often leaves with additional electrons.
- $Nu: + R:L \rightarrow R:Nu^{+} + :L^{-}$

  Neutral nucleophile *substrate* *product* *leaving group*
- $Nu:^{-} + R:L \rightarrow R:Nu^{+} + :L^{-}$

  Anion nucleophile *substrate* *product* *leaving group*

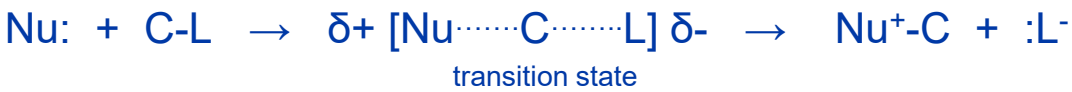
Example


$CH_3CH_2O:^-Na^+ + CH_3CH_2Br \rightarrow CH_3CH_2OCH_2CH_3 + Na^+Br^-$
Anion-nucleophile
substrate
product
leaving group

S_N2 Mechanism

- Substitution nucleophilic reaction requiring two reactants (nucleophile + substrate)
- 1 step reaction
- The nucleophile “attacks” the substrate at the carbon and the leaving group – well it leaves :) and when it leaves it carries with it its electron pair.

S_N2 Mechanism



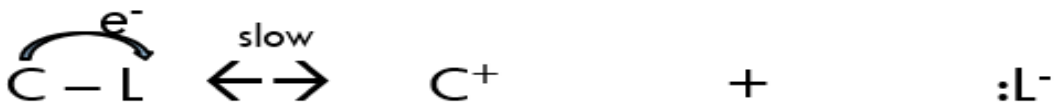
- S_N2 reactions can be identified by:
- The rate of the reaction depends on concentration of both nucleophile and substrate.
- The displacement results in an inversion of configuration. (R ⇆ S)
- The reaction is fastest when alkyl group of substrate is primary; slowest when tertiary (or not at all).

S_N1 Mechanism

Substitution nucleophilic reaction requiring one initial reactant (the substrate) in the first step.

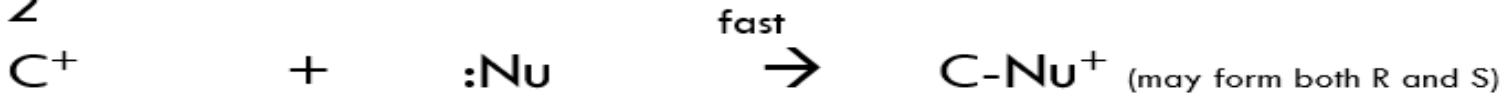
2 step reaction

STEP 1



Substrate carbocation leaving group

STEP 2



Carbocation nucleophile product

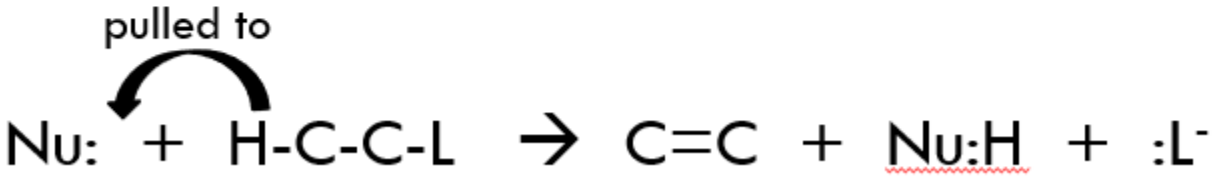
S_N1 Mechanism

- SN1 Mechanism can be identified by:
  - 1. The rate of reaction is NOT dependent on the concentration of nucleophile.
  - 2. If the carbocation is asymmetric the reaction will result in a racemic mixture (& loss of optical activity).
  - 3. Fastest when alkyl group of the subtrate is tertiary, slowest if primary.

Elimination Reactions

- E2 – one step

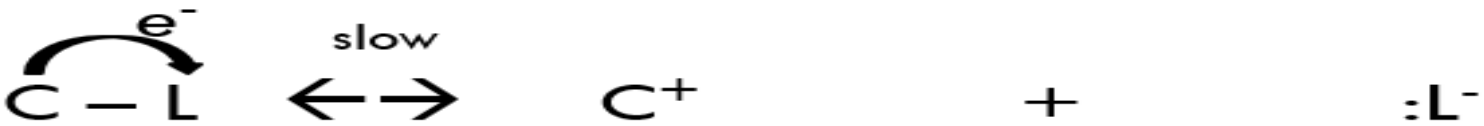
The nucleophile removes the proton (hydrogen) on the carbon adjacent to the leaving group, simultaneously the leaving group breaks off and a double bond is formed.



Elimination Reactions

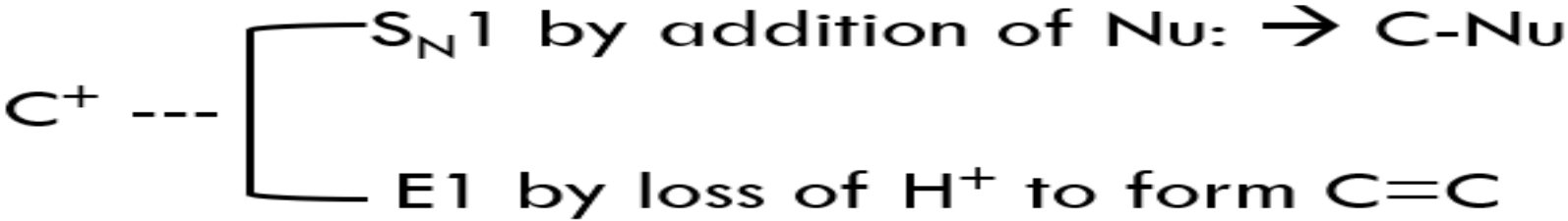
E1 — two step

STEP 1



Substrate carbocation leaving group

STEP 2 — can finish as S_N1 or lose H^+



Substitution vs. Elimination Competition

- Tertiary Carbocations favor S_N1
- Secondary Carbocations – depends on type of nucleophile:
  - strong nucleophile favors S_N2
  - weak nucleophile Major: S_N1 Minor: E1
  - strong base Major: E2 Minor: S_N2
- Primary Carbocations mainly favor S_N2, but can use E2 with strong bases

2021 National Exam

56. Which is the best explanation for the higher reactivity of conjugated dienes relative to non-conjugated alkenes in electrophilic addition reactions?

(A) Conjugated dienes can form allylic cations on reaction with electrophiles while non-conjugated alkenes cannot.

(B) Conjugated dienes have more potentially reactive sites than do non-conjugated alkenes.

(C) The π bonding in conjugated dienes is weaker than the π bonding in non-conjugated alkenes.

(D) Conjugated dienes are nonplanar while non-conjugated alkenes are planar.

2017 National Exam

58. What is the role of the acid catalyst in the Fischer esterification reaction below?

(A) Shifts the equilibrium in the right-hand direction

(B) Neutralizes the base formed as a side product in the reaction

(C) Converts ethanol to a more reactive nucleophile

(D) Converts propanoic acid to a more reactive electrophile