1. Suppose Schrodinger owned a big, fluffy cat that appeared black under sunlight. If the cat was placed in a room that was illuminated with only green light, what colour would the cat appear?

absorbs all visible wavelengths

A) Red
B) Black
C) Violet
D) Green
E) White

2. How many of the photophysical processes listed below change the magnetic properties of a molecule (i.e. from diamagnetic to paramagnetic, or from paramagnetic to diamagnetic)?

diamagnetic = no net spin (singlet)

- Absorption $S_0 \rightarrow S_1$
- Vibrational cooling
- Fluorescence $S_1 \rightarrow S_0$
- Intersystem crossing $S_1 \rightarrow T_1$

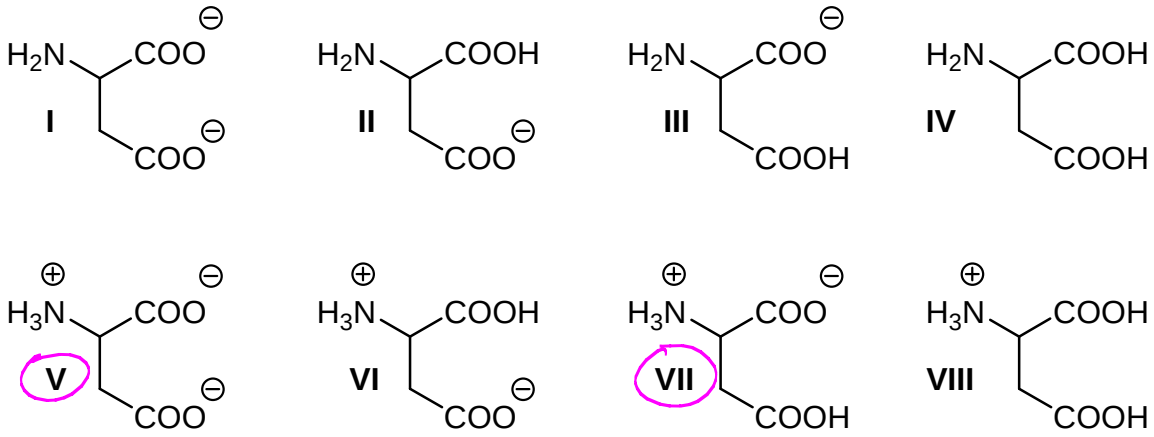
paramagnetic = net spin (triplet)

A) None
B) 4
C) 2
D) 3
E) 1

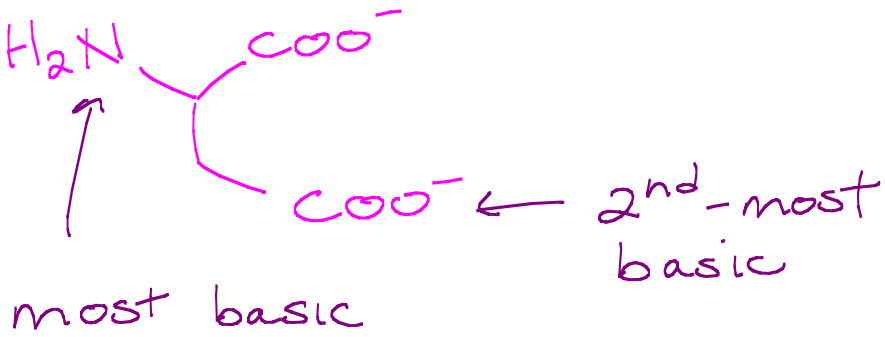
3. The outer membrane of Gram-negative bacteria is primarily composed of…

A) Peptidoglycan
B) Lipopolysaccharide
C) Glycoprotein
D) Nucleic acid
E) Mucopolysaccharide

4. 1.5 mol of HCl were added to 1.0 mol of disodium aspartate dissolved in distilled water. The resulting solution contains an approximately equal concentration of which two structures?




A) **III** and **IV**
B) **V** and **VI**
C) **VI** and **VIII**
D) **V** and **VII**
E) **II** and **III**



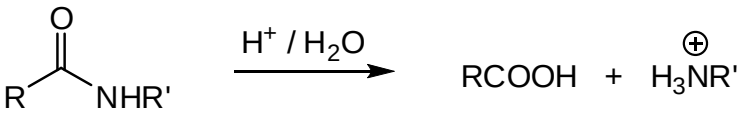
5. Both the protonated and unprotonated forms of the imidazole group of histidine can be detected by UV-visible spectroscopy. If histidine was dissolved in a buffer, and measurements indicated that 50% of the imidazole groups were protonated, what is the approximate pH of the buffer?

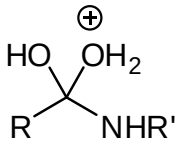
pH = pKa when 1:1 of acid : base

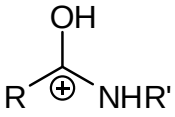
A) 3
B) 10
C) 14
D) 6
E) 2

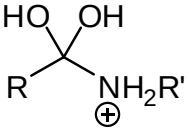
6. Which one of A – E is *least likely* to be involved in the mechanism of the following reaction?

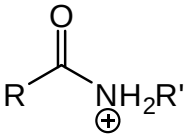
work out mechanism

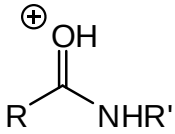



**A)** 

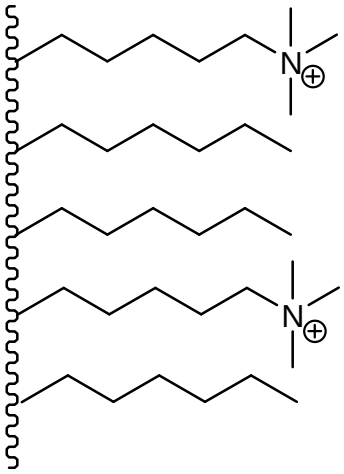

**B)** 


**C)** 


**D)** 


**E)** 

7. A mixture of amino acids, predominantly in the net-charge forms listed below, was injected into an HPLC chromatography column consisting of a hydrophobic stationary phase with quaternary ammonium groups (see diagram). Predict the order of elution of the amino acids, from first to last.




*stationary phase material*

*mixture of amino acids:*

Lysine (net charge of positive one)

Alanine (net charge of zero)

Glycine (net charge of zero)

Leucine (net charge of zero)

Aspartic acid (net charge of negative one)

| | **first** → | | | | **last** |
|---|---|---|---|---|---|
| **A)** | Aspartic acid | Leucine | Alanine | Glycine | Lysine |
| **B)** | Glycine | Leucine | Aspartic acid | Lysine | Alanine |
| **C)** | Lysine (+) | Glycine | Alanine | most Leucine hydrophobic | Aspartic acid (−) |
| **D)** | Lysine | Leucine | Alanine | Glycine | Aspartic acid |
| **E)** | Aspartic acid | Alanine | Glycine | Leucine | Lysine |

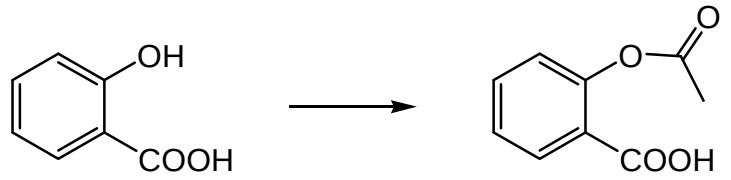
8. What is the purpose of DCC in peptide synthesis?

A) It protects the carboxylic acid and prevents it from reacting
B) It converts the carboxylic acid into a more-reactive acid derivative
C) It assists in the protection of the amino group
D) It protects the side chains of the amino acids from reacting
E) It converts the amino group into a better nucleophile

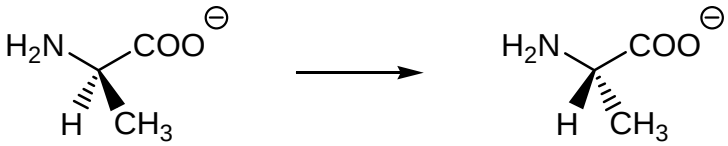
9. In which reaction is the starting material behaving in a *prochiral* manner?

achiral → chiral

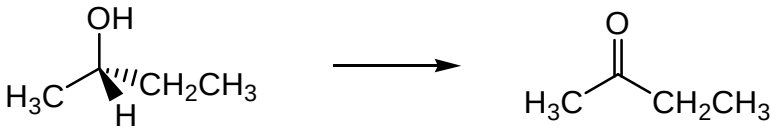
**A)**



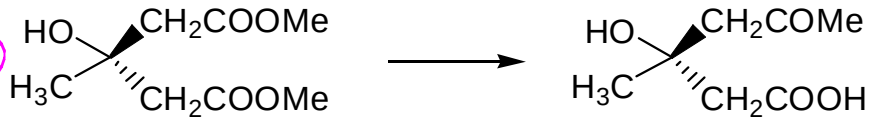

**B)**



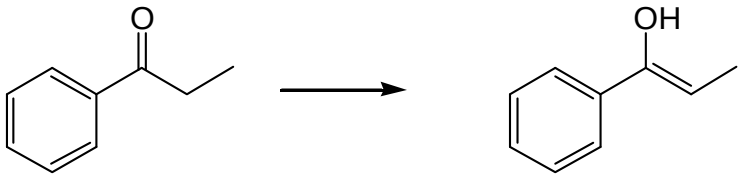

**C)**



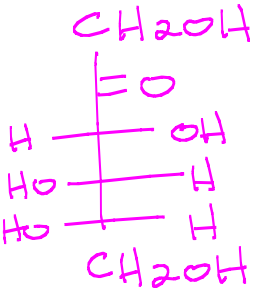

**D)**



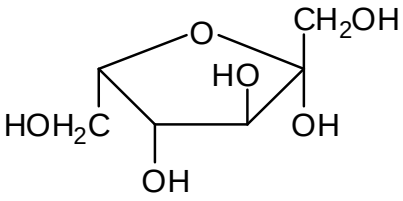

**E)**



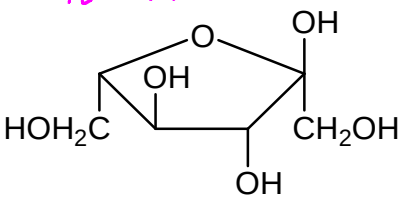
10. Which one of the following is β-L-fructose?



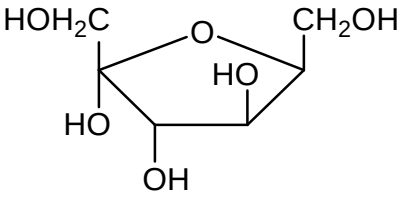

**A)**



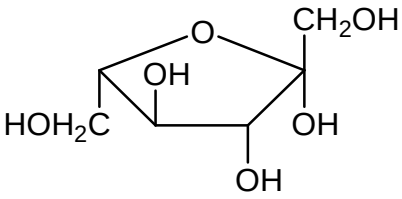

**B)**



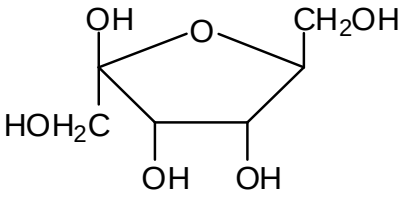

**C)**



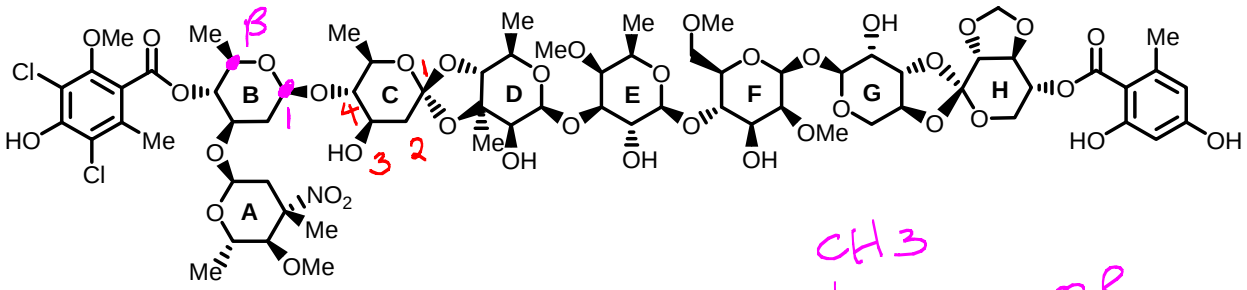

**D)**

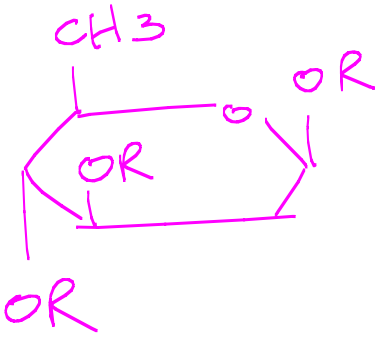



**E)**



The next two questions are based on the natural product *everinomycin* (shown below), which has promising activity against antibiotic-resistant bacteria. The sugar-derived rings of *everinomycin* are labelled **A** through **H**.




11. From which sugar is ring **B** derived?

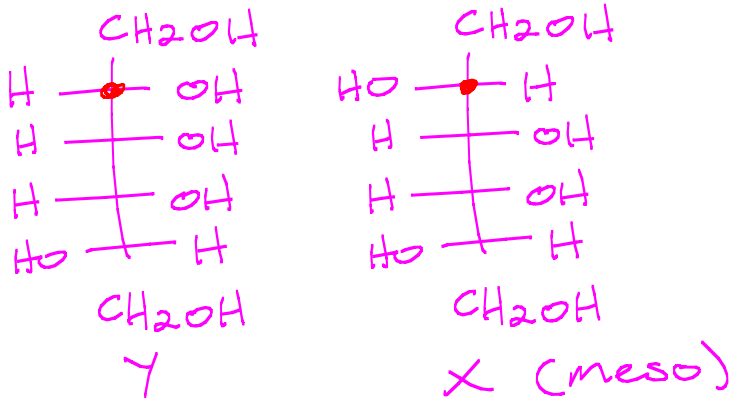
A) 2,6-dideoxy-L-mannose
B) 2,6-dideoxy-L-idose
C) 6-deoxy-D-fructose
D) 2,6-dideoxy-D-altrose
E) 2,6-dideoxy-D-glucose

12. What type of linkage is used to connect ring **B** to ring **C**?

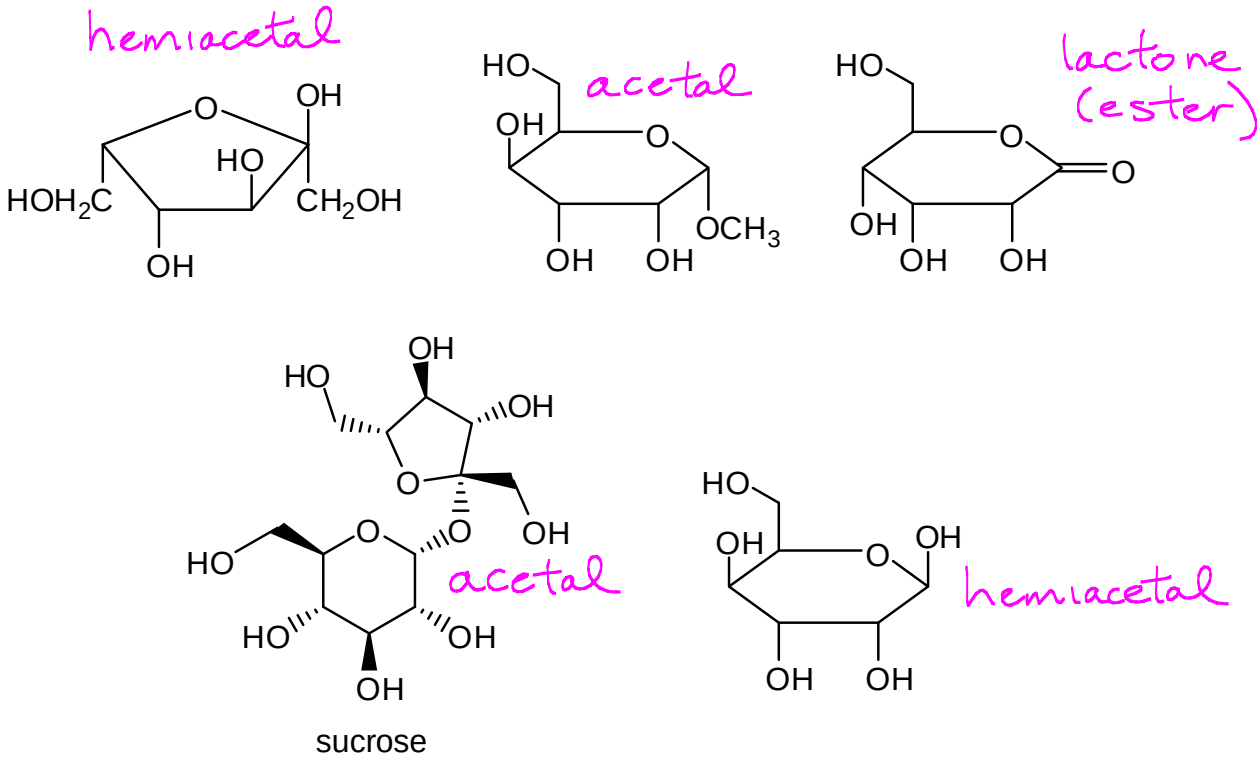
A) α(1,4)
B) α(3,1)
C) β(1,4)
D) α(1,3)
E) β(4,1)

13. Reduction of L-tagulose with $H_2$/Pt forms equal amounts of two products, **X** and **Y**. Product **X** is optically inactive. Similar reduction of which one of A – E would give product **Y** as the only product?

A) D-Talose
B) D-Sorbose
C) L-Altrose
D) L-Psicose
E) D-Psicose




14. How many of the following compounds can form an acyclic (non-cyclic) structure when treated with an aqueous base, such as NaOH?

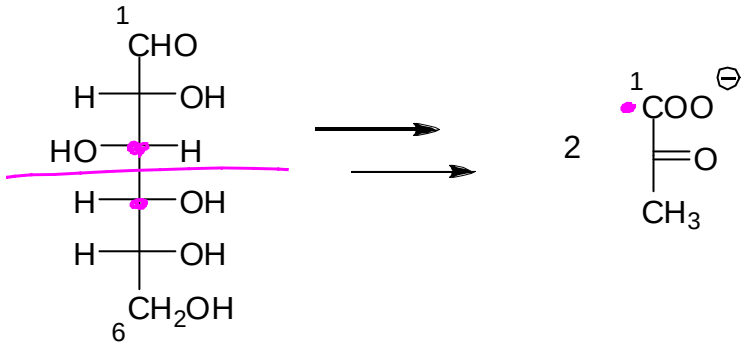



sucrose

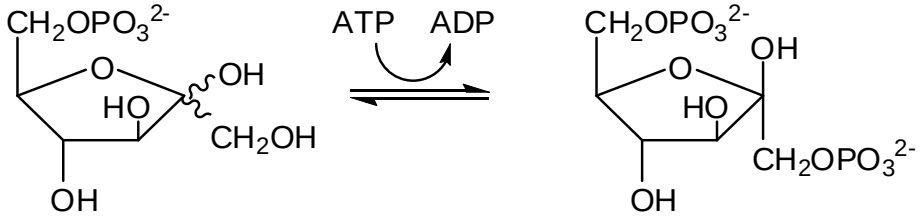
A) 3
B) 2
C) 5
D) 1
E) 4

15. In glycolysis, one mole of glucose is converted into two moles of pyruvate. From which carbon atoms in glucose is carbon 1 of pyruvate derived?

A) 1 and 4
B) 1 only
C) 3 and 6
D) 3 and 4
E) 1 and 6



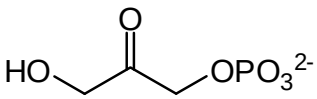

16. The enzyme *phosphofructokinase* catalyzes the phosphorylation of fructose-6-phosphate. Which statement best explains why the enzyme forms only the β-anomer of fructose-1,6-bisphosphate as the product?



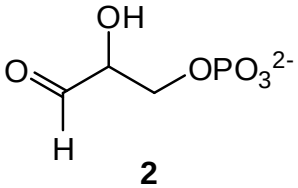

mixture of anomers

A) The product is actually produced as a mixture of anomers, but it equilibrates so that only the β-anomer is present.
B) Both anomers are produced, but ATP inverts the anomer to the other one.
C) When glucose-6-phosphate isomerizes to fructose-6-phosphate, only the β-anomer is produced.
D) The enzyme acts on only the β-anomer of fructose-6-phosphate.
E) Phosphofructokinase degrades the undesired anomer to other products.

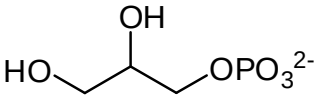
17. The enzyme *aldolase* catalyzes a retroaldol reaction of fructose-1,6-bisphosphate. Which of the following are the products of the reaction?



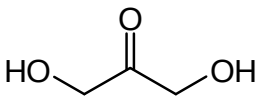

**1**



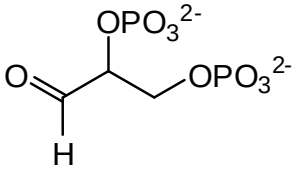

**2**




**3**

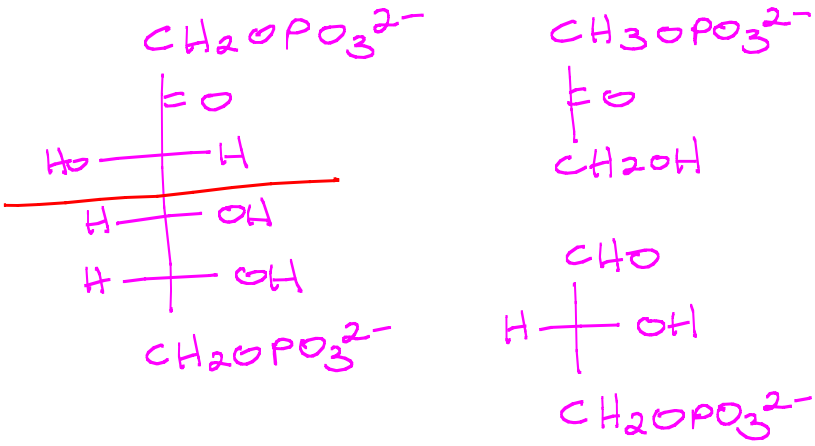



**4**

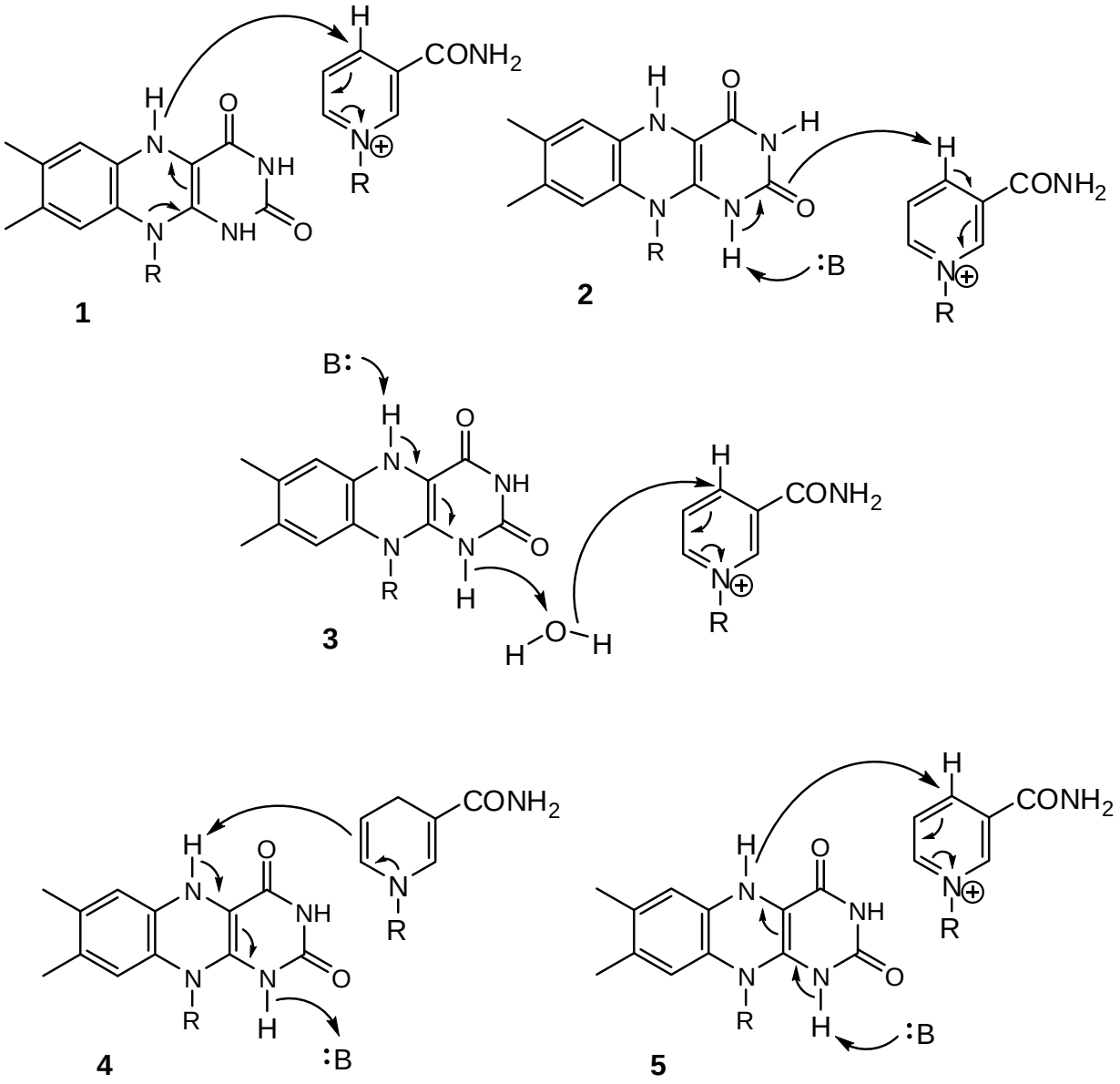



**5**

A) 1 and 2
B) Two molecules of 2
C) 1 and 3
D) Two molecules of 1
E) 4 and 5

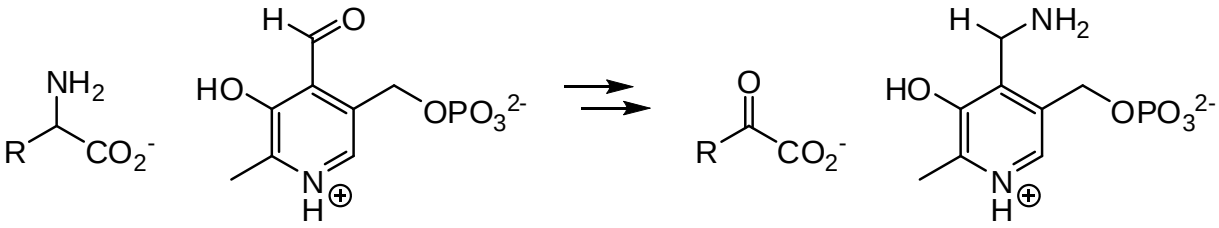


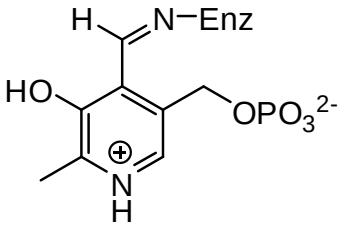
18. $FADH_2$ can react with $NAD^+$ to form FAD and NADH. Which one of A – E correctly shows this enzyme-catalyzed reaction?



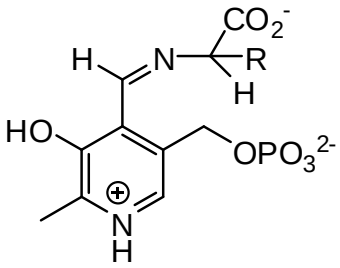

A) 4
B) 5
C) 2
D) 3
E) 1

19. Consider the enzymatic reaction of pyridoxal phosphate with an amino acid to form an α-keto acid. Which is NOT an intermediate in this process?

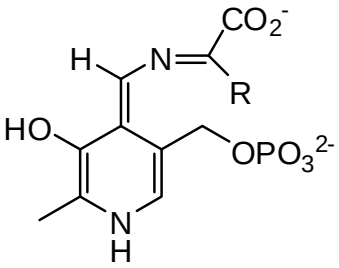




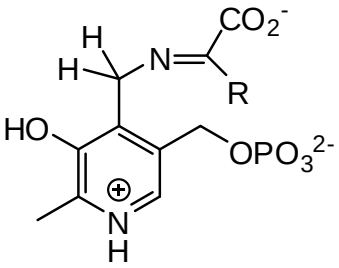
**1**



**2**



**3**



**4**

A) 3

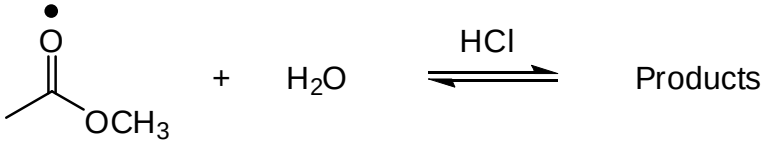
B) 2

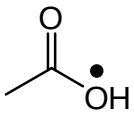
C) They are all intermediates

D) 1

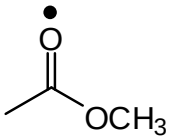
E) 4

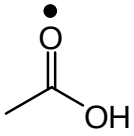
20. The isotopically labelled ester below was combined with water in the presence of catalytic HCl. Which one of A – E is *least likely* to be found in the reaction mixture at equilibrium?




**A)** 


**B)** $CH_3OH$

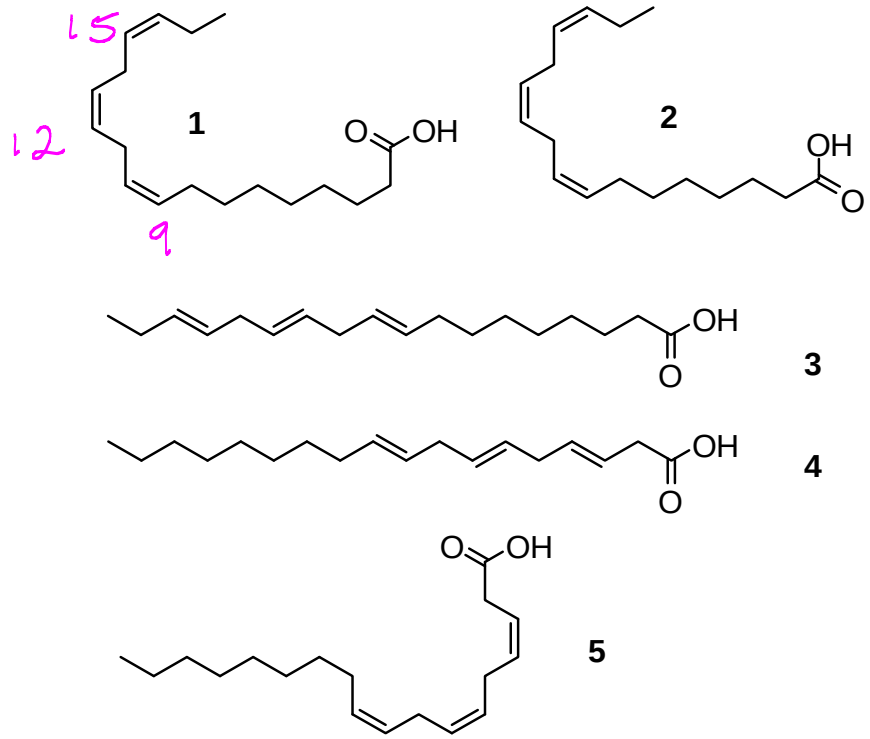
**C)** 


**D)** 


**E)** $CH_3\dot{O}H$

$CH_3$-O bond is not broken during the reaction

21. Alpha linolenic acid is a naturally occurring $C_{18}\Delta^{9,12,15}$ fatty acid. Which of the following is alpha linolenic acid?




A) **4**

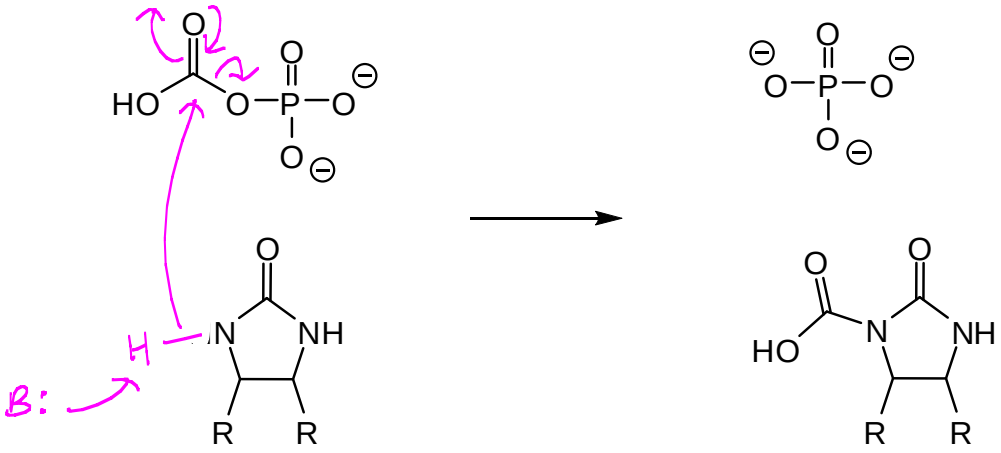
B) **1**

C) **5**

D) **2**

E) **3**

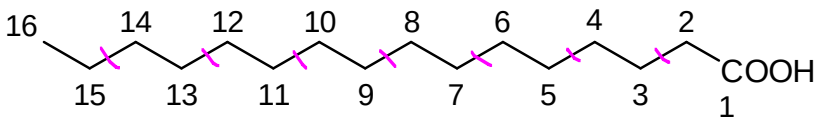
22. Consider the reaction of biotin with carboxyphosphate to form carboxybiotin. Which statement(s) is/are correct?



1. A carbon atom acts as an electrophile
2. Phosphate is the leaving group
3. A tetrahedral intermediate is formed during the reaction

A) 2 only
B) 1 and 2 only
C) 1 only
D) 2 and 3 only
E) All statements are correct

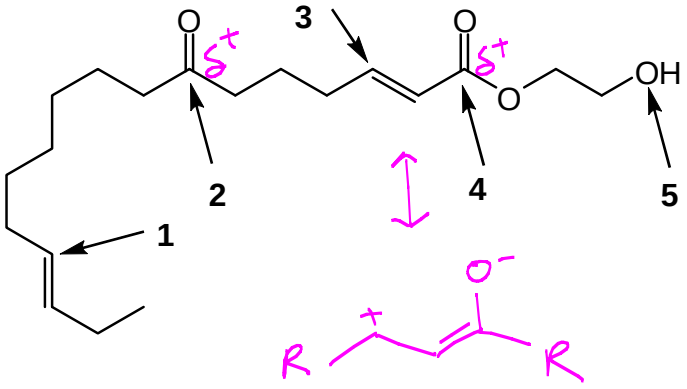
23. Which statement regarding palmitic acid, shown below, is correct?




7 bonds made

A) A double bond was reduced between C3 and C4.
B) The bond between C6 and C7 was formed in the third Claisen reaction.
C) The even-numbered carbons were, at one time, reduced by NADPH.
D) Seven equivalents of ATP were required to synthesis this fatty acid.
E) Carbon 1 came from carbon dioxide.

24. In the compound below, only which of the indicated atoms is/are electrophilic?




A) **5**

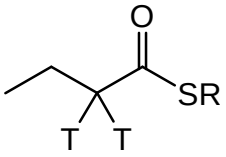
B) **2** and **4**

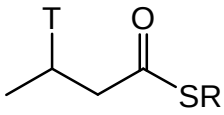
C) **2**, **3**, and **4**

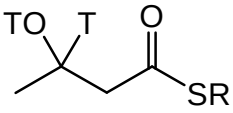
D) **1**, **2**, **3**, and **4**

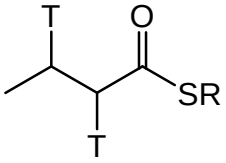
E) **1** and **3**

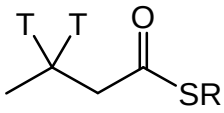
25. *Nicotinamide adenine dinucleotide phosphate reduced form* labelled with tritium ($^3$H = T) in place of all hydrogens was combined with unlabelled acetyl-CoA and all of the other reagents and enzymes necessary for fatty-acid biosynthesis. What is formed after one round of fatty-acid biosynthesis? (Assume that all *nicotinamide adenine dinucleotide phosphate reduced form* present is labelled)

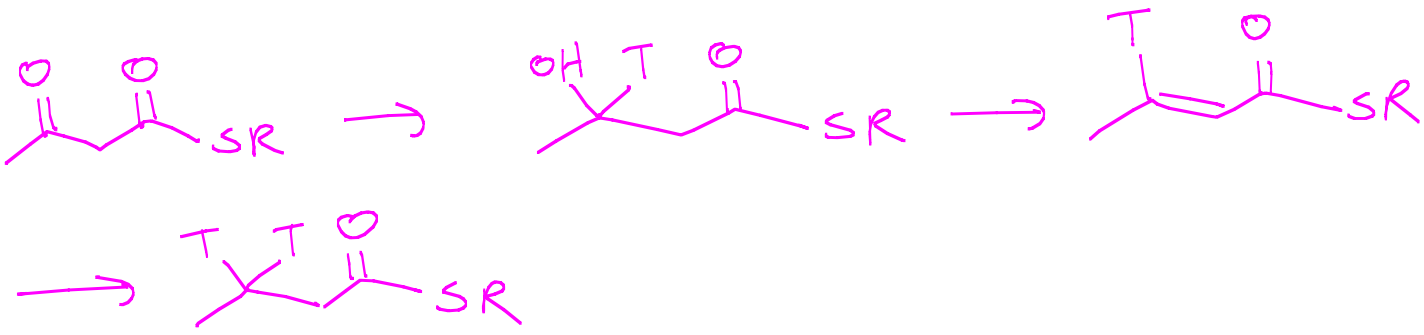
**A)** 


**B)** 

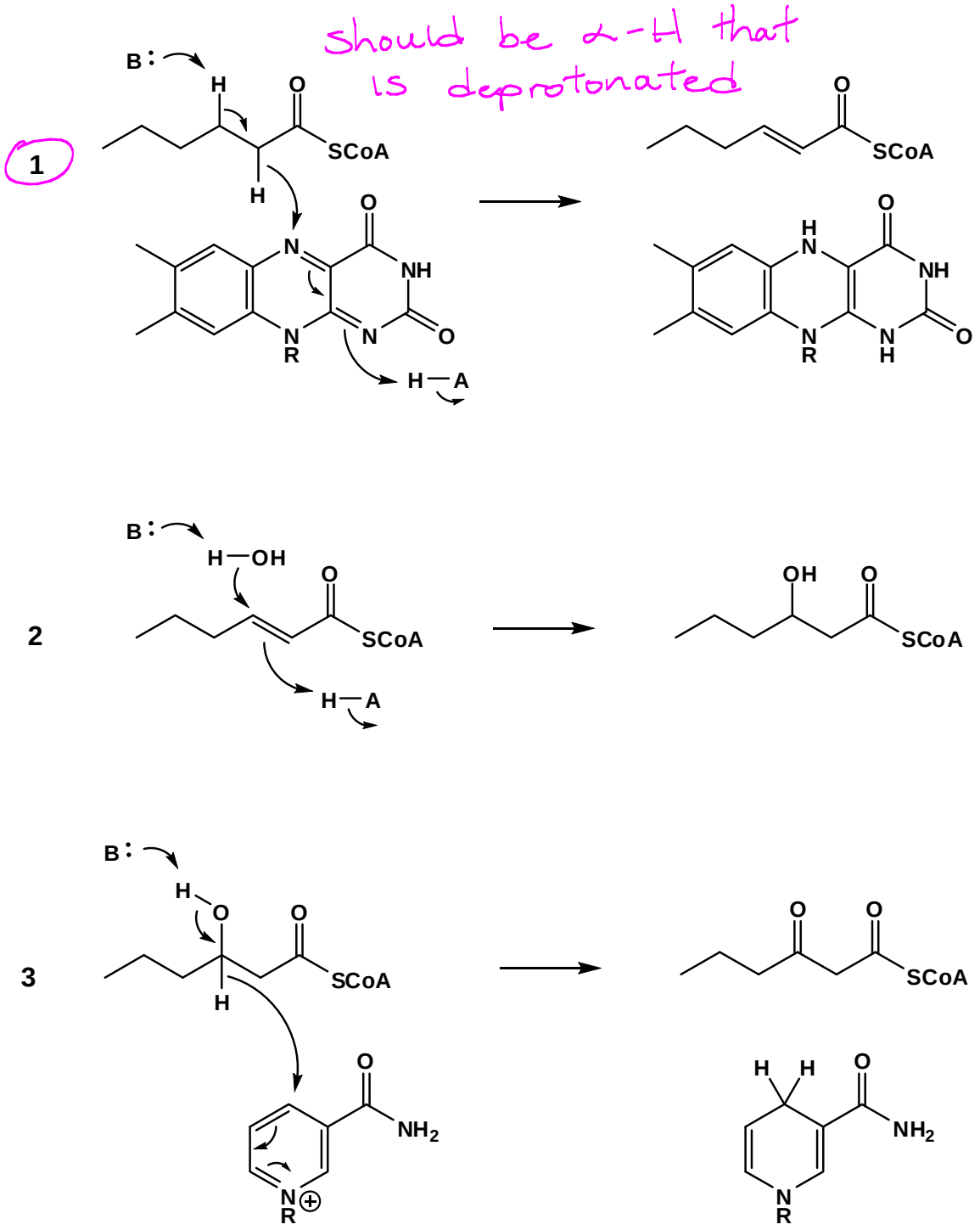

**C)** 


**D)** 

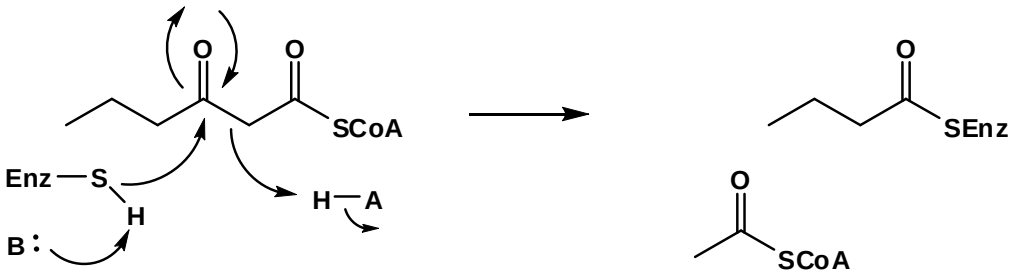

**E)** 

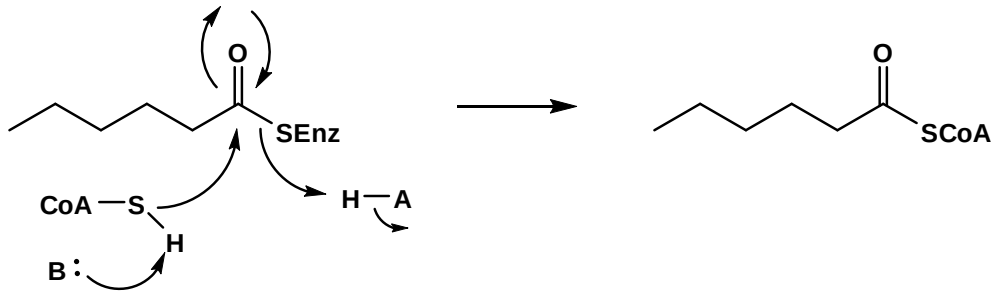
26. The β-oxidation process is shown below. Which mechanistic step is incorrect? (Note that this question spans two pages)



**4**




**5**




A) **3**

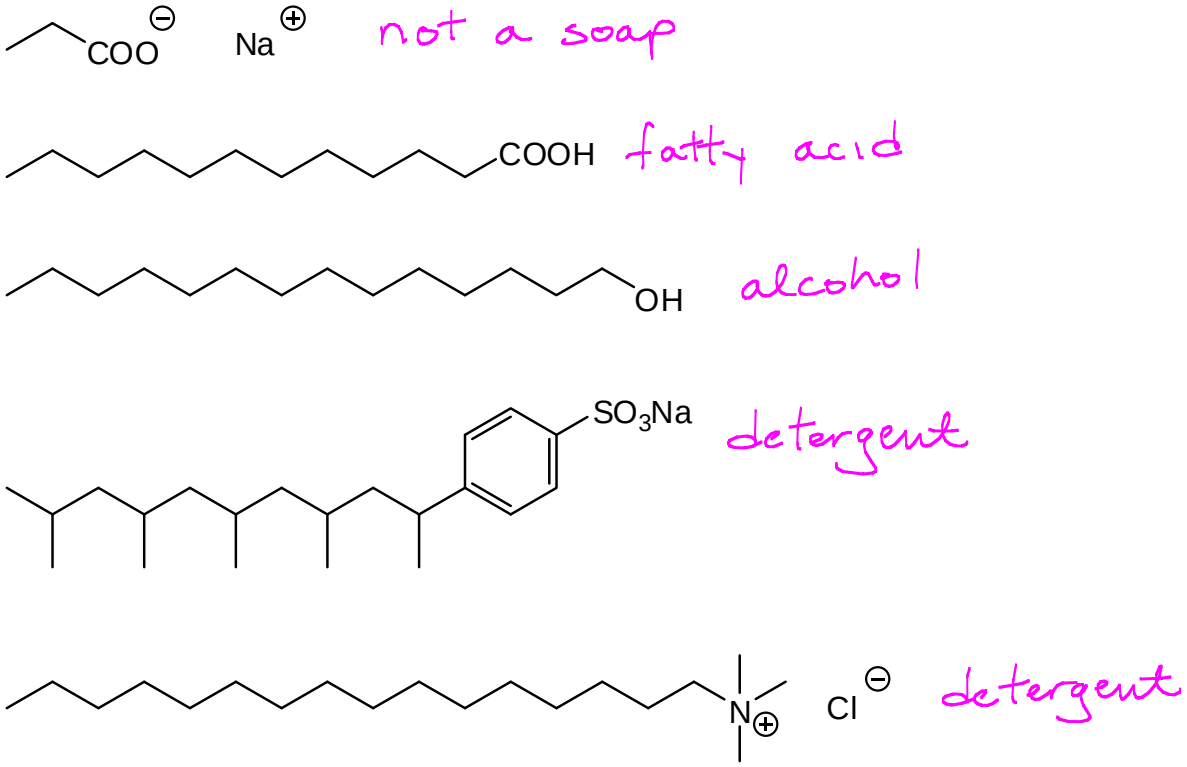
B) **5**

C) **2**

D) **1**

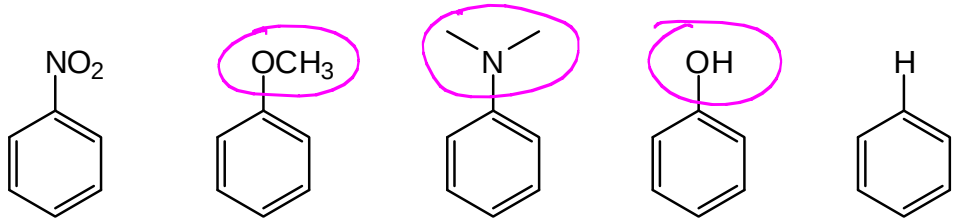
E) **4**

27. How many of the following compounds are expected to be good cleaning agents in hard water?




A) 5
B) 4
C) 1
D) 2
E) 3

28. How many of the following aromatic compounds contain an *ortho/para* director?




EDG groups

A) 2
B) 4
C) 5
D) 3
E) 1

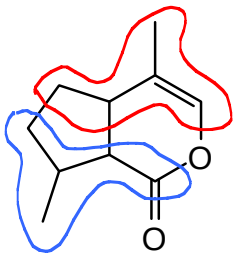
29. How many of the following are nucleophilic acyl substitution reactions?

- Aldol reaction nu. addn.
- Cyclization of an ketose into a hemiacetal nu. addn.
- Reaction an aldehyde with NADH nu. addn.
- Claisen reaction
- Reaction of an amino acid with dinitrofluorobenzene nu. aromatic subs.

A) 2
B) All of them
C) 3
D) 4
E) 1

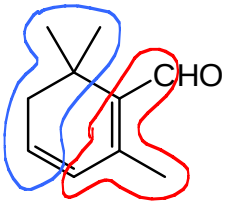
30. Which one of the following does NOT obey the isoprene (terpene) rules?

**A)**



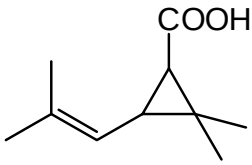

nepetalactone (catnip)

**B)**



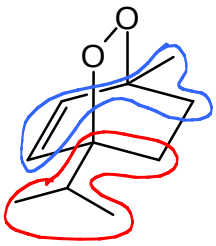

**safranal (saffron)**

**C)**



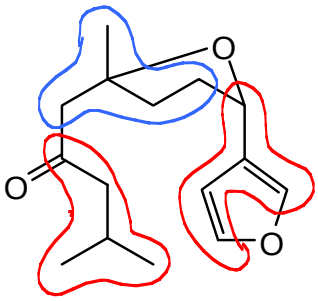

chrysanthemic acid (chrysanthemum flowers)

**D)**



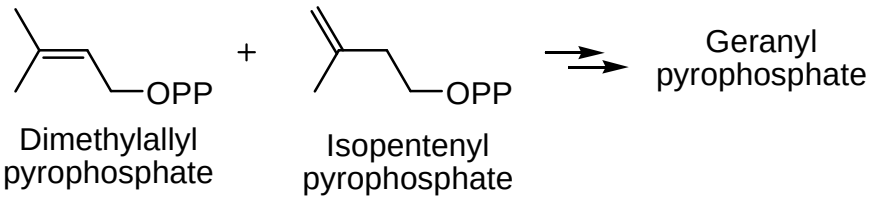

ascaridole (boldo plant)

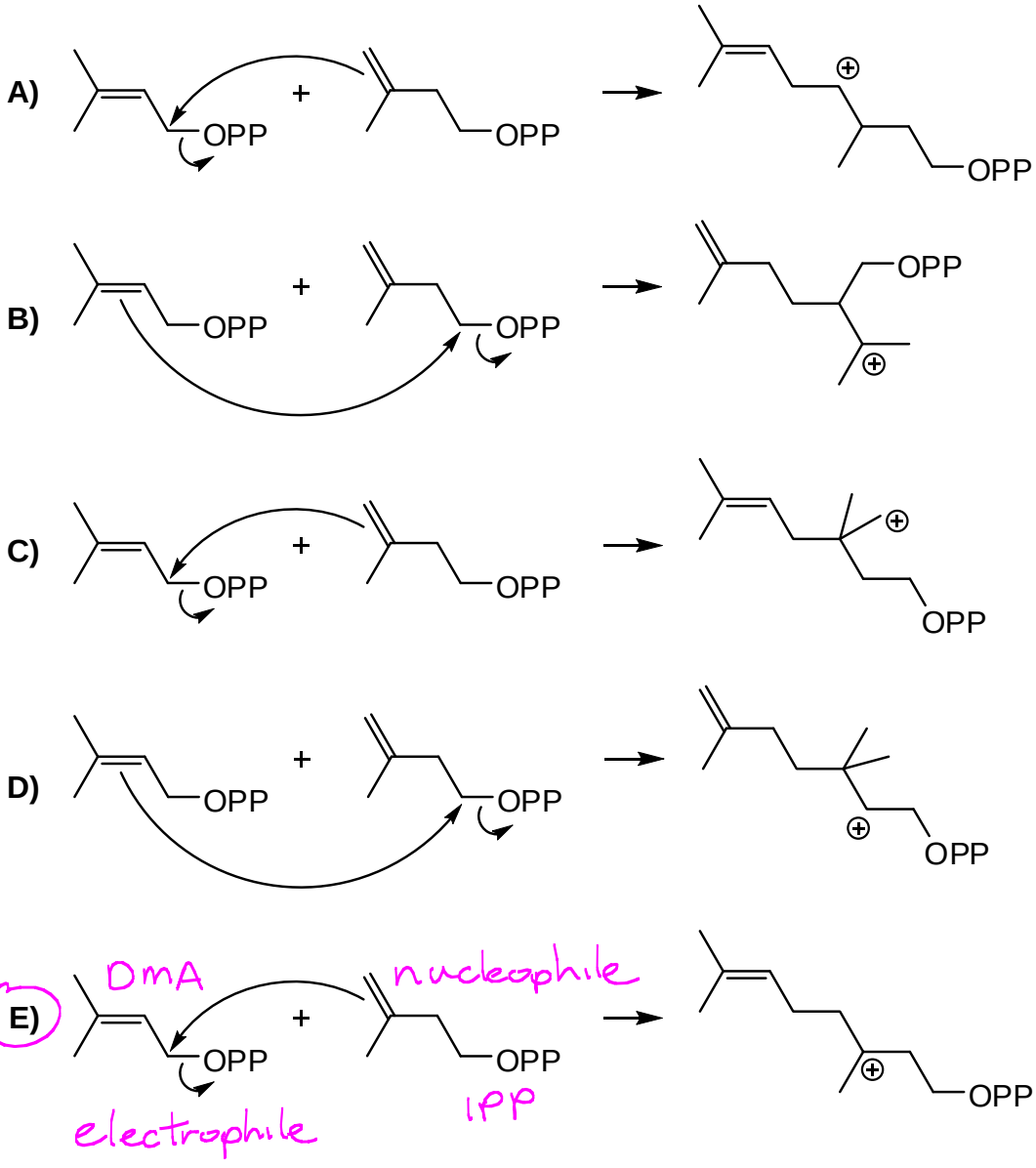
**E)**



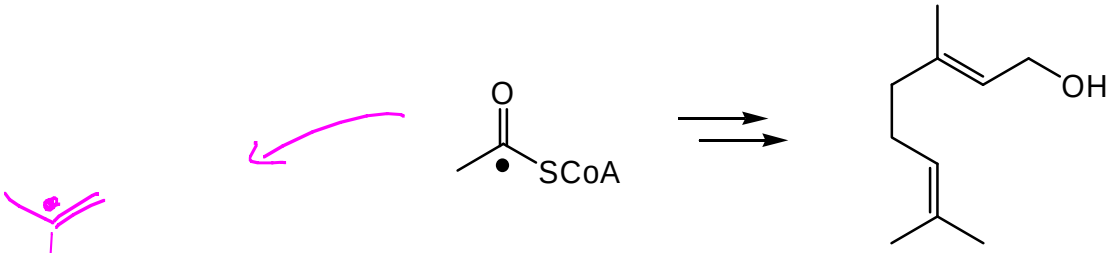

ipomeamarone (potato fungus)

31. The biosynthesis of geranyl pyrophosphate involves the reaction of dimethylallyl pyrophosphate with isopentenyl pyrophosphate to form a new C-C bond. Which one of A – E correctly shows this reaction?



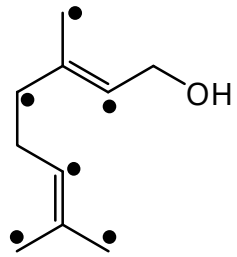



32. The compound below is a terpene isolated from roses. It can be biosynthesized exclusively from acetyl-CoA that is isotope-labelled at the C-1 (indicated by a dot). Which one of A – E shows the correct locations of the isotope?

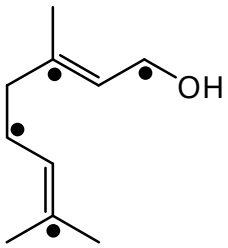




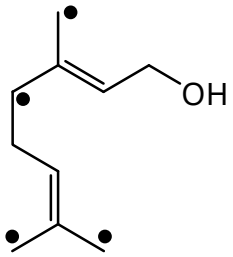
**A)**



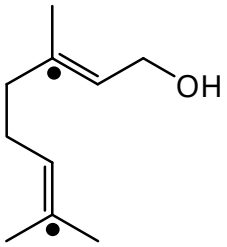

**B)**



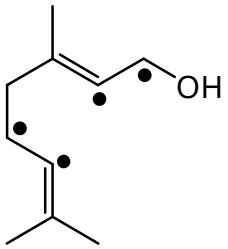

**C)**




**D)**

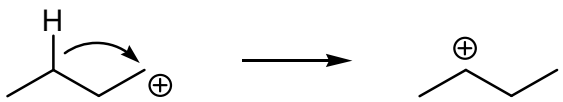



**E)**

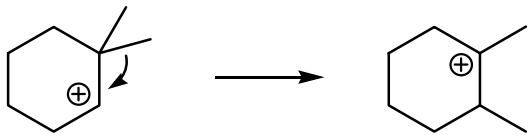


33. Which one of A – E is a correct mechanistic representation of a 1,2-hydride shift?

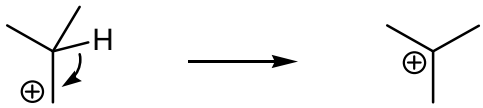
**A)**



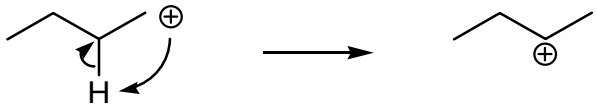

**B)**



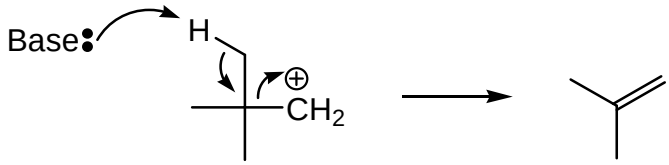
**C)**




**D)**

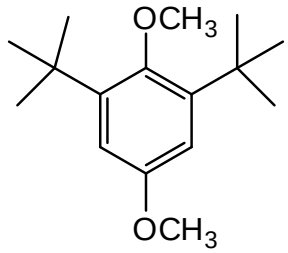


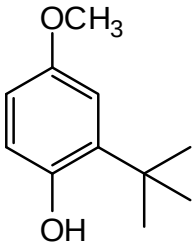

**E)**

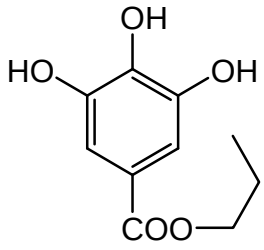


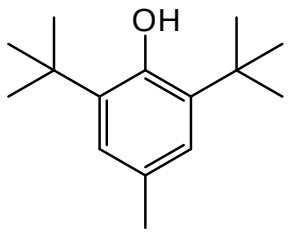
34. Some compounds that act as antioxidants function in a mechanistic manner similar to that of Vitamin E, and these are often used as food preservatives. Which one of the following is NOT expected to function like vitamin E?

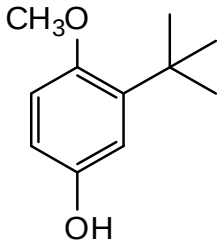
phenolic OH group

**A)** 


**B)** 

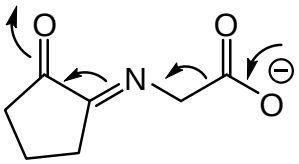

**C)** 

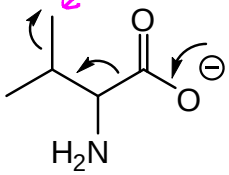

**D)** 

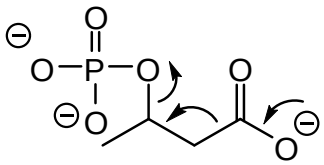

**E)** 

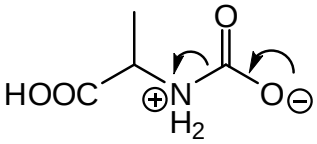

35. Which one of the following decarboxylation reactions is *least likely* to proceed according to the mechanism drawn?

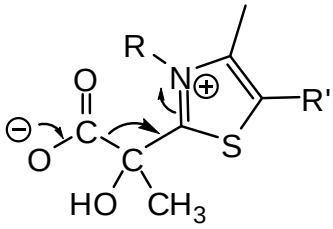
bad leaving group

**A)** 

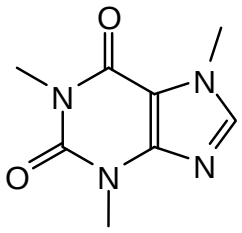

**B)** 


**C)** 

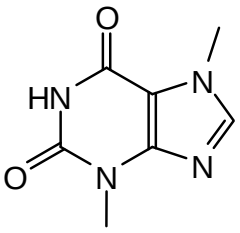

**D)** 


**E)** 

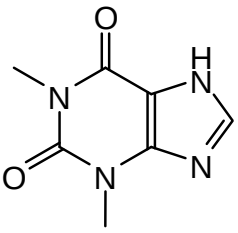
36. How many of the following molecules are classified as pyrimidines?



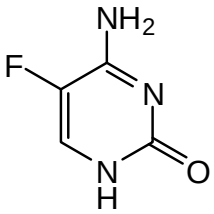
**caffeine**
stimulant in coffee



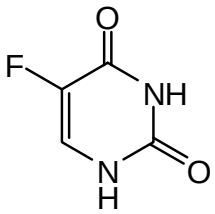
**theobromine**
stimulant in chocolate



**Quibron ®**
anti-asthmatic



**Ancobon ®**
anti-fungal



**Fluoroblastin ®**
anti-cancer

A) 5

B) 1

C) 3

D) 4

E) 2

37. In nucleic acids, *intercalation* is best defined as which one of the following?

A) The insertion of hydrogen bonds between bases on adjacent strands

B) The insertion of an extra nitrogen atom into the ring structure of purines

C) The insertion of an extra day into a specific month to allow the calendar to match the solar year

D) The insertion of a large, flat molecule between the stacked base pairs

E) The insertion of thymine-thymine crosslinkages

38. Which one of the following statements is NOT correct?

A) Exposure to UV light can result in the formation of T-T dimers in DNA via a photocycloaddition reaction.

B) The wavelength of UV-A light is longer than the wavelength of UV-C light.

C) Compounds that are classified as carcinogenic are often not carcinogenic themselves, but rather, their metabolites are the true carcinogenic species.

D) Polyaromatic hydrocarbons are formed while fat burns at a high temperature.

E) A compound with a higher $LD_{50}$ is ~~more~~ less toxic.

39. Which one of A – E correctly lists the sequence of events and thermocycler temperatures for one cycle of the polymerase chain reaction?

**A)** 1. Annealing at 72 °C
2. Elongation at 54 °C
3. Melting at 94 °C

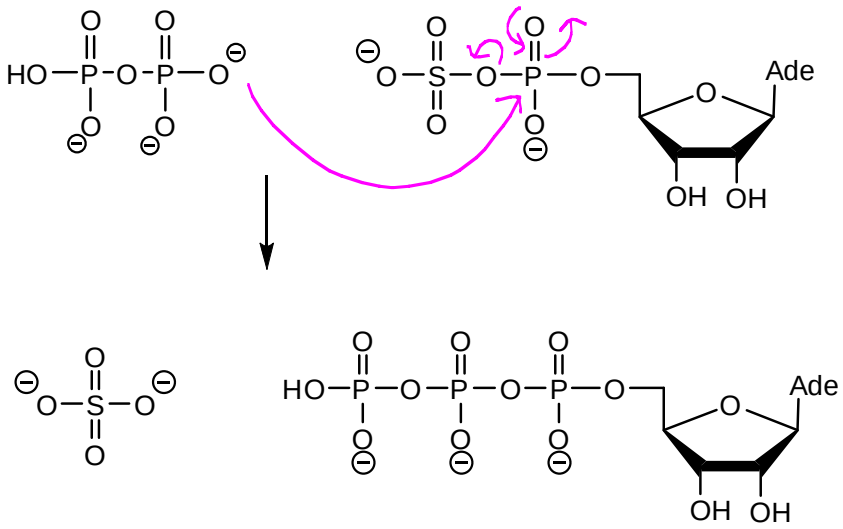
**B)** 1. Melting at 72 °C
2. Annealing at 54 °C
3. Elongation at 94 °C

**C)** 1. Melting at 94 °C
2. Elongation at 72 °C
3. Annealing at 54 °C

**D)** 1. Annealing at 54 °C
2. Melting at 94 °C
3. Elongation at 72 °C

**E)** 1. Melting at 94 °C
2. Annealing at 54 °C
3. Elongation at 72 °C

40. In pyrosequencing, ATP sulfurylase catalyzes the conversion of adenosine 5'-phosphosulfate into ATP. Which statement(s) is/are CORRECT?




1. Pyrophosphate is the nucleophile
2. ~~ATP~~ is the leaving group sulfate
3. An intermediate with a pentavalent (trigonal bipyramidal) ~~sulfur~~ P atom is formed during the reaction

A) 1 and 2 only

B) All of 1, 2, and 3

C) 2 and 3 only

D) 1 only

E) 2 only

41. Which statement regarding solid-phase DNA synthesis is NOT correct?

A) The DNA strand is synthesized (elongated) from the 3' end to the 5' end.

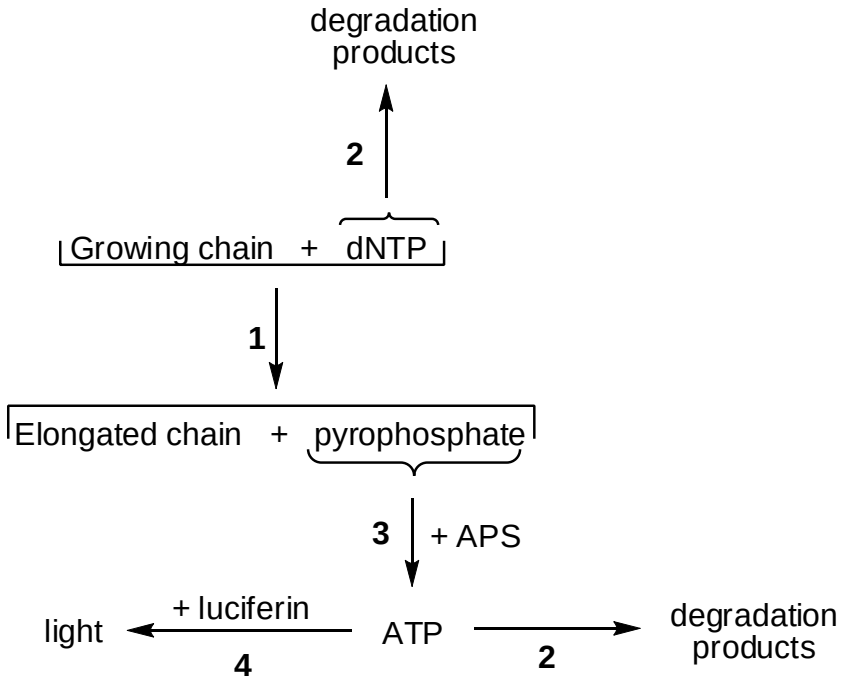
B) The DNA product, which is linked to the insoluble polymer as an ester, is cleaved using ammonia in a nucleophilic acyl substitution reaction.

C) The maximum length of an oligonucleotide that can be synthesized with high yield is dependent on the efficiency of the steps involved in the cycle.

D) The oxidizing agent converts the phosphorus atom from a +3 oxidation state to a +5 oxidation state.

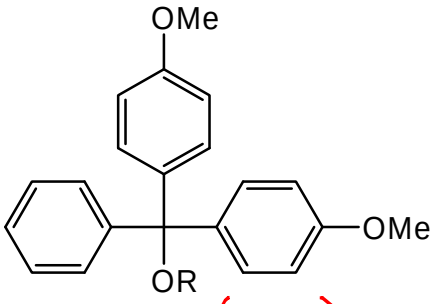
E) The β-cyanoethyl group bonded to the phosphate is removed by ~~acid~~ base hydrolysis.

42. Shown below are the relevant reactions involved in pyrosequencing. In order for pyrosequencing to work, the reactions must occur at different rates. Which one of A – E ranks the reaction rates, from slowest to fastest, in a manner that allows pyrosequencing to work most efficiently?



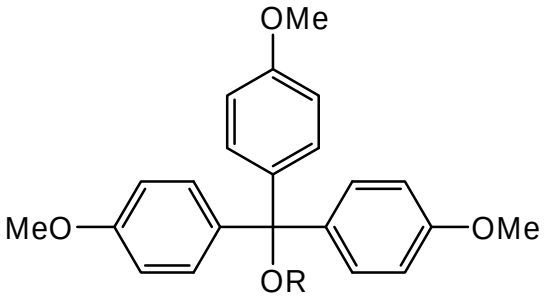

| | Slowest | → | | Fastest |
|---|---|---|---|---|
| A) | 1 | 2 | 4 | 3 |
| B) | 3 | 1 | 4 | 2 |
| C) | 4 | 1 | 3 | 2 |
| D) | 3 | 4 | 2 | 1 |
| E) | 2 | 3 | 1 | 4 |

43. Rank the following compounds in the order of decreasing acid lability, from the most acid-labile to the least acid-labile.

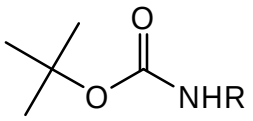



(TCA)

I

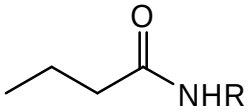



II



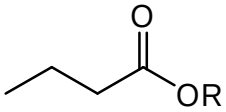

III

carbamate (TFA removal)




IV

amide




V

ester (HBr/HOAc removal)

| | most | | | | least |
|---|---|---|---|---|---|
| **A)** | **V** | **IV** | **II** | **I** | **III** |
| **B)** | **IV** | **V** | **II** | **I** | **III** |
| **C)** | **II** | **III** | **I** | **V** | **IV** |
| **D)** | **I** | **II** | **III** | **V** | **IV** |
| **E)** | **II** | **I** | **III** | **V** | **IV** |

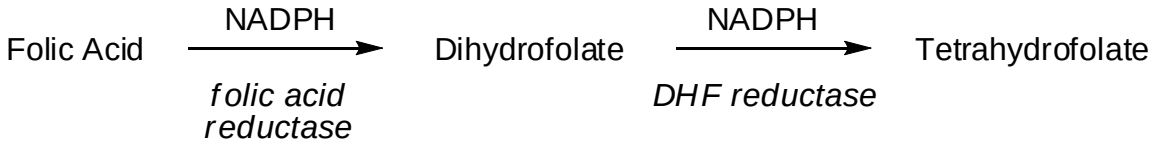
44. Which one of the following is the weakest acid?

A) Tetrazole
B) Trichloroacetic acid
C) Trifluoroacetic acid
D) HBr
E) HCl

45. In the United States, the pharmaceutical-drug approval process is regulated by the FDA. Which organization in Canada performs the same function as the FDA?

A) Canada Revenue Agency
B) Natural Health Products Directorate
C) Canada Border Services Agency
D) Health Canada
E) Liquor Control Board of Ontario

46. In the body, folic acid is enzymatically reduced to tetrahydrofolate in two steps.




A few years ago, a large recall of pet food was initiated by an Ontario-based company. It was first suspected that the food contained *aminopterin*, a DHF reductase inhibitor and a potent rat poison.

Given that aminopterin is a substrate analog that competes with dihydrofolate for the DHF reductase active site, thereby preventing dihydrofolate from binding, aminopterin could also be classified as which one of the following?

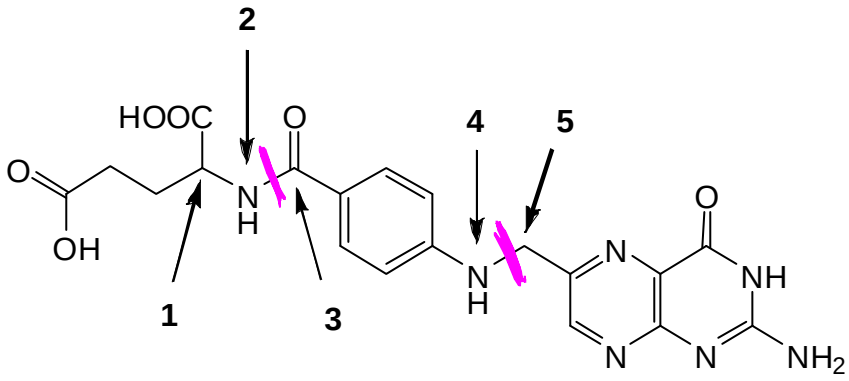
A) Substrate analog of tetrahydrofolate
B) DHF reductase antagonist
C) Substrate analog of folic acid
D) Tetrahydrofolate antagonist
E) Inhibitor of folic acid reductase

47. For a drug to act as a substrate analog, it must…

A) Have the same toxicity has the natural substrate
B) Have the same pKa as the natural substrate
C) Have a size and shape similar to that of the natural substrate
D) Have the efficacy as the natural substrate
E) Have the same number of hydrogens as the natural substrate

48. During the biosynthesis of folic acid from glutamic acid, *p*-aminobenzoate, and the pteridine derivative, two coupling reactions took place. Which two carbon and/or nitrogen atoms acted as *electrophiles* during the biosynthesis?

A) 2 and 4
B) 3 and 4
C) 2 and 5
D) 1 and 5
E) 3 and 5




49. In photodynamic therapy, why is it important to use a photosensitizer that absorbs at a long wavelength?

A) Photosensitizers that absorb at a short wavelength are too expensive.
B) Ground-state molecular oxygen has the highest absorption at long wavelengths.
C) Tissue contains very few natural chromophores that absorb at long wavelengths, allowing the light to travel deeper into the tissue.
D) Long wavelengths in the IR region are required to vibrationally excite oxygen.
E) The high energy of long-wavelength light creates reactive oxygen species that are more cytotoxic than those generated with short-wavelength light.

50. Which one of the following is NOT a *reactive oxygen species*?

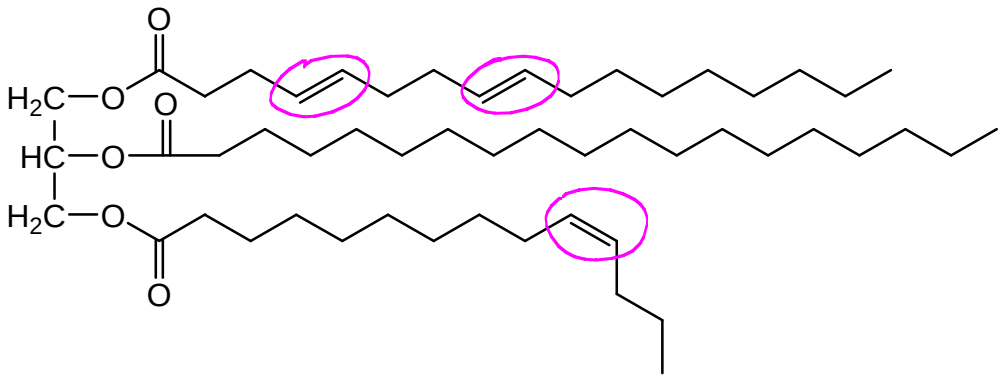
A) $O_2^-$
B) HO•
C) HOO•
D) $^3O_2$ ← ground-state oxygen
E) $H_2O_2$

51. Benedict's test could be used to distinguish between which two compounds?

A) Fructose and tagulose
B) Mannose and fructose
C) None of other answers are correct
D) Glucitol and psicose
E) Sucrose and mannitol

ketoses give a positive test

52. One mole of the triglyceride shown below will decolourize how many moles of bromine dissolved in dichloromethane?



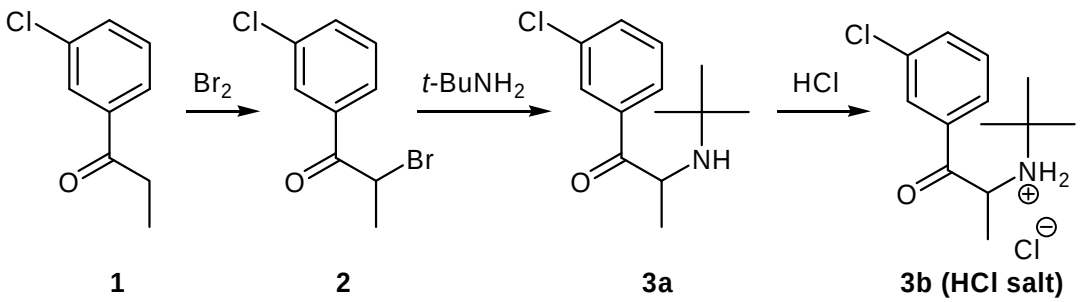
A) 3
B) 2
C) 4
D) 6
E) 1

53. When detergents are dissolved in water, the pH of the resulting solution is close to neutral, while soap solutions are alkaline. Which statement best explains this phenomenon?

A) Soaps precipitate in the presence of $Ca^{2+}$.
B) Detergents are typically sulfate or sulfonate salts.
C) Detergents contain less unsaturation than soaps.
D) Soaps are carboxylic acids, which are soluble in bases.
E) Detergents are made from natural oils and fats, which are not basic.

salts of strong acids are not basic

54. Regarding the one-pot synthetic scheme for Zyban, which statement is correct?




**1** **2** **3a** **3b (HCl salt)**

A) The conversion of **1** to **2** is classified as a β-bromination.

B) Compound **3b** is soluble in ether.

C) Using *N*-methylpyrrolidinone as the solvent, the conversion of compound **2** to **3a** is occurs by an $S_N1$ reaction mechanism.

D) Compound **3a** can be separated from leftover **1** and **2** by performing an ether/water extraction.

E) The conversion of **1** to **2** involves an autocatalytic process.

55. Refer again to the one-pot synthetic scheme in Question 54. During the synthesis, which compound was collected in the Hickman still head?

A) Compound 3a

B) Compound 3b

C) Compound 1

D) Compound 2

E) None of other answers are correct (one pot!)

*Answers to this final exam will NOT be posted. Unofficial course grades will be posted to your WebCT gradebook. Enjoy your summer!*