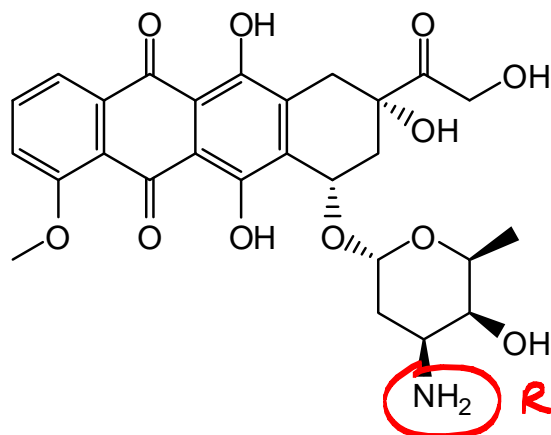


1. The term *auxochrome* is best defined as, or described by, which one of A – E?

- A) Substances or objects that are coloured
- B) The subtractive colour model and our perception of colour
- C) The vibrational cooling that occurs after a molecule absorbs light
- D) How different colours are separated on a TLC plate
- E) Functional groups or parts of molecules that modify the light-absorption properties of a chromophore**

2. Which statements are correct about doxorubicin, a red anticancer agent?



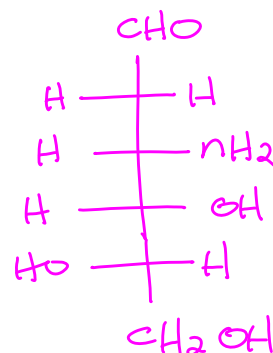
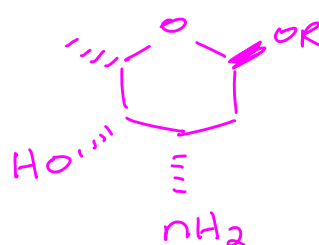
- 1. Doxorubicin contains the benzoquinone chromophore ✓
- 2. Doxorubicin is red in colour because it absorbs green light ✓
- 3. At neutral pH, in solution, doxorubicin would exist as a zwitterion ✗

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

3. Referring to the structure of doxorubicin, which carbohydrate is present in its structure?

- A) 1,3,4-Trideoxy-3-amino-D-glucose
 B) 1,3,4-Trideoxy-3-amino-L-arabinose
 C) 3-Amino-2,3,6-trideoxy-D-arabinose
 D) 4-Amino-3,4,6-trideoxy-L-galactose
 E) 3-Amino-2,3,6-trideoxy-L-galactose

redraw:

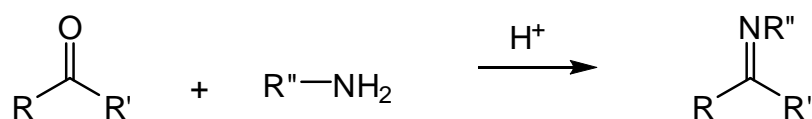


4. The pKa of the protonated side chain of histidine is 6.0. At what pH would the side chain of histidine have an average charge of +0.50?

- A) 12.0
 B) 3.0
 C) 5.5
 D) 6.5
 E) 6.0

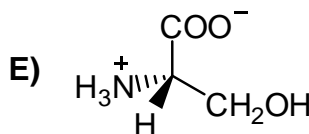
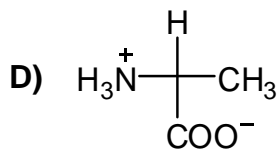
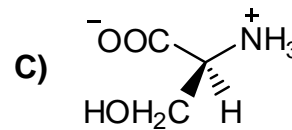
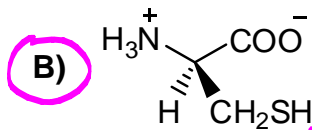
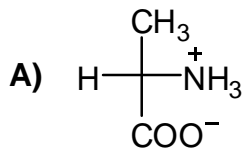
50% neutral (base form)
 50% +1 (acid form)
 when pH = pKa

5. This reaction is best described as a...



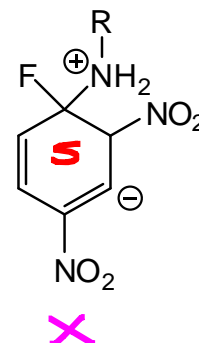
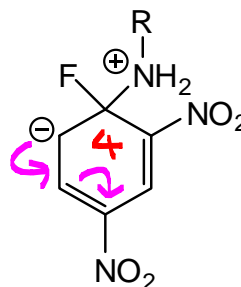
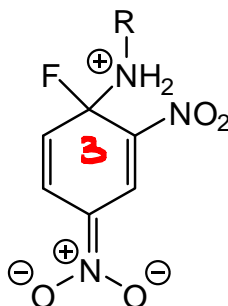
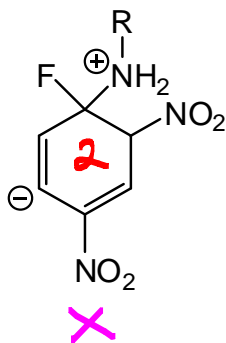
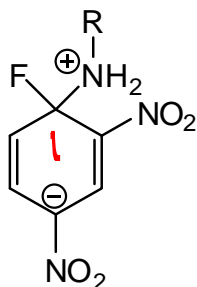
- A) S_N2 substitution
 B) Nucleophilic acyl substitution
 C) S_N1 substitution
 D) Nucleophilic addition
 E) Electrophilic substitution

6. Which one the following amino acids is *least likely* to be naturally occurring?



build model to see that this is a D-amino acid

7. How many of the following are NOT contributing structures of the intermediate formed during the reaction of Sanger's reagent (dinitrofluorobenzene) with the N-terminal amino acid of a polypeptide (R)?



A) 1

B) 3

C) 2

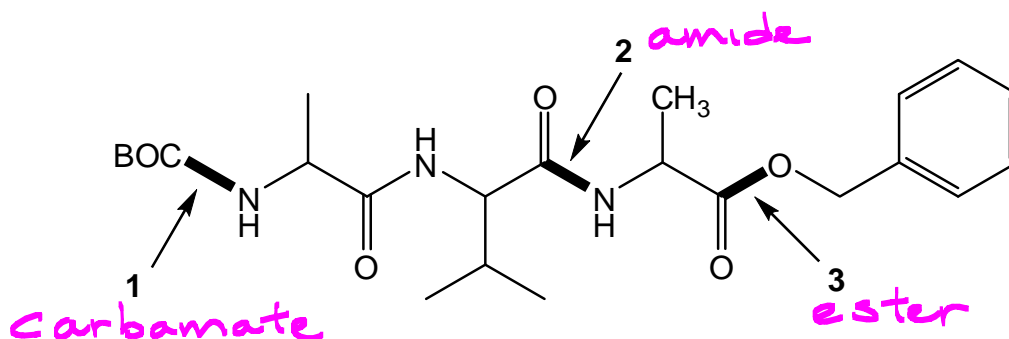
D) 4

E) None (all are contributing structures)

- move e⁻ shown in 4 to get 1

- ~~4~~ gives 3

8. Rank the indicated connections shown in the compound below in the order of increasing acid lability, from the least acid-labile to the most acid-labile.



	Least	→	Most
A)	1		2
B)	3		1
C)	1		3
D)	2		1
E)	2		3

9. Consider the hydrolysis of an amide under acidic conditions. Which one of A – E is most likely to be correct about the mechanism?

- A) The reaction proceeds via an S_N2 mechanism.
- B) Acid protonates water to make it a better nucleophile.
- C)** Acid protonates the oxygen atom of the carbonyl group to make the carbon of the carbonyl group a better electrophile. *acid activates C=O*
- D) Water is deprotonated to make it a better nucleophile.
- E) The leaving group is protonated after its departure from the acyl carbon so that it becomes as a neutrally charged species.

10. The side chains of how many of the following amino acids are non-nucleophilic?

Lysine

Glutamine

Valine

Phenylalanine

A) 1

B) 3

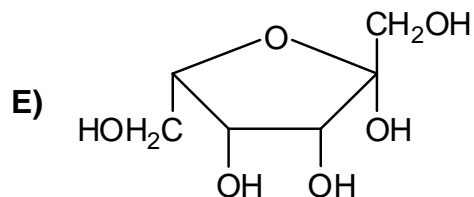
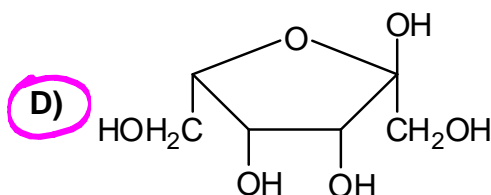
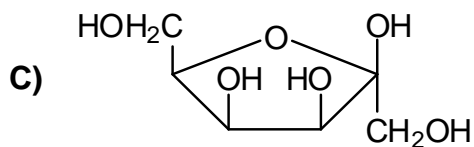
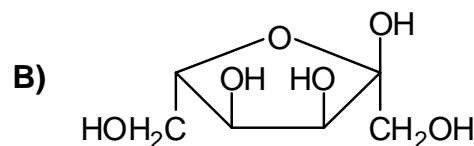
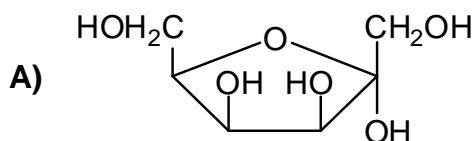
C) None (all contain nucleophilic side chains)

D) 4

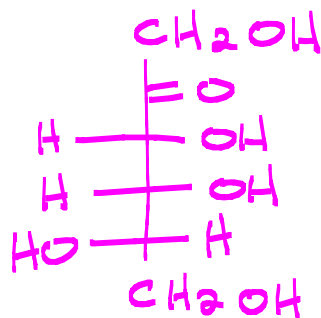
E) 2

N lone pair delocalized by resonance

11. Which one of the following is α -L-tagulose?



Start from Fischer projection of L-tagulose



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

- A) D-Glyceraldehyde must be dextrorotatory, and L-glyceraldehyde must be levorotatory.
- B) D-Glucose and L-glucose are enantiomers.
- C) D-Gulose and D-glyceraldehyde have the same configuration at the penultimate carbon.
- D) D-Glucose and D-gulose have the same configuration at the penultimate carbon but different configurations at carbon 4.
- E) D-Glucose and D-mannose are anomers. ~~anomers~~ *epimers*

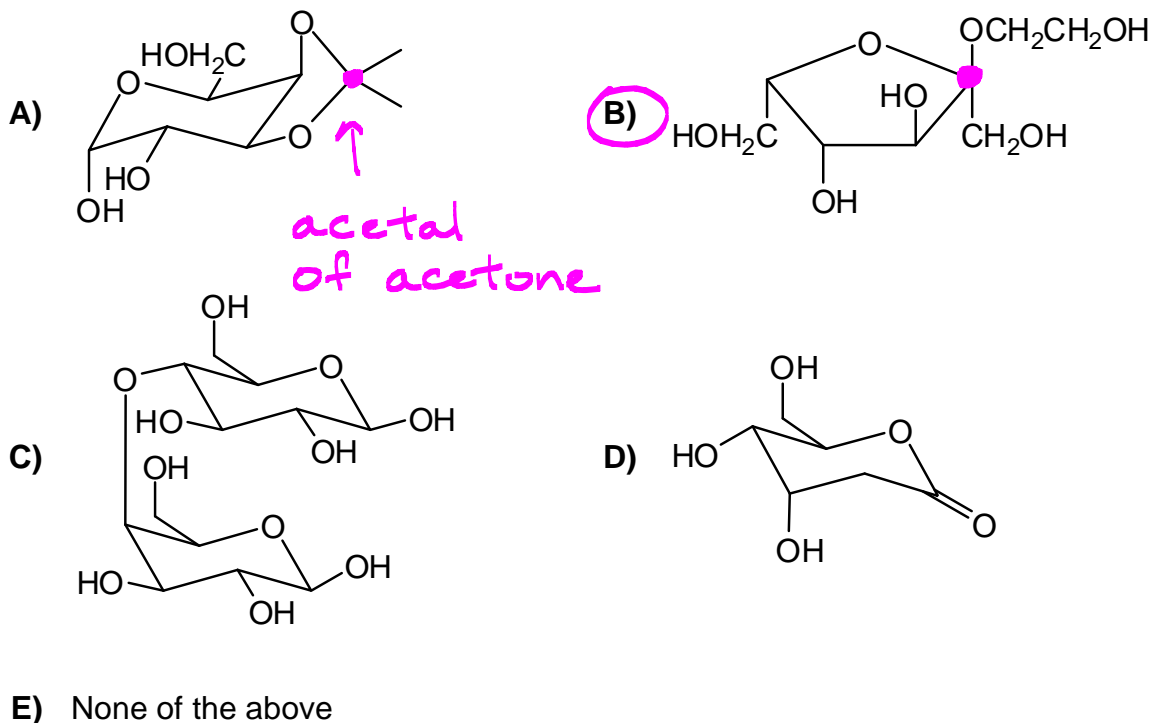
13. How many stereoisomers of aldoheptoses in the open-chain form are possible?

- A) 32 *2⁵*
 - B) 16
 - C) 64
 - D) 4
 - E) 8
- ↖ 5 chiral centres*

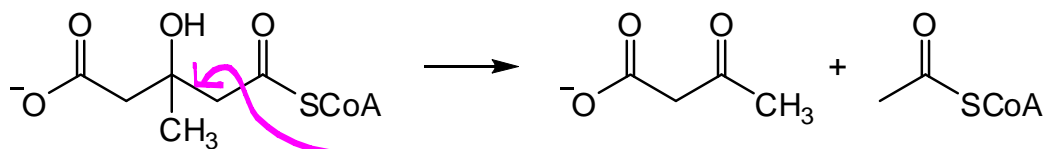
14. How many of the following are reducing sugars *and* can be reduced by NaBH₄?

- Lactose *✓*
 - Fructose *✗*
 - Glucose *✓*
- aldose*
- A) 3
 - B) 2
 - C) 1
 - D) None of them, because reducing sugars cannot be reduced any further.
 - E) None of them, because reducing sugars are oxidizing agents.

15. Which one of the following is a glycoside? ✓ acetal of sugar

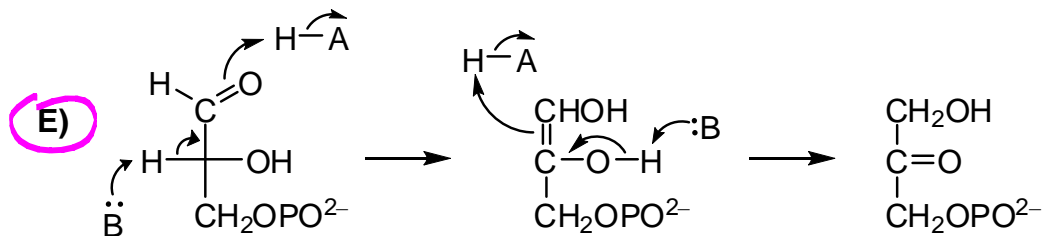
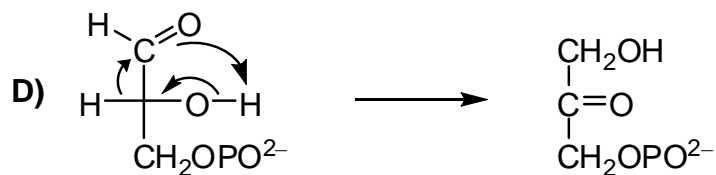
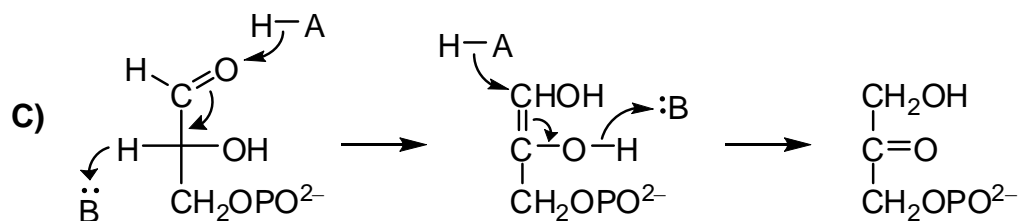
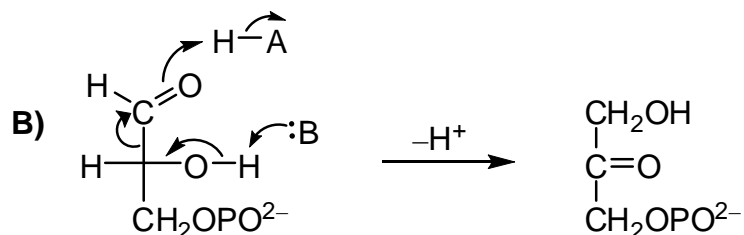
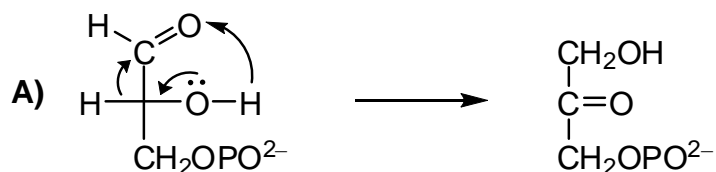


16. The enzyme *3-hydroxy-3-methylglutaryl-CoA lyase* catalyzes the cleavage reaction below. This reaction is best described as a...



- α, β linkage cleaved
(reverse of adding
α-carbanion to C=O)
- A) Nucleophilic acyl substitution
 B) Claisen condensation
 C) Retro-Michael reaction
 D) E2 elimination
 E) Retro-aldol reaction

17. Which of A – E is a correct mechanism for the enzyme-catalyzed isomerization of glyceraldehyde-3-phosphate to dihydroxyacetone phosphate?

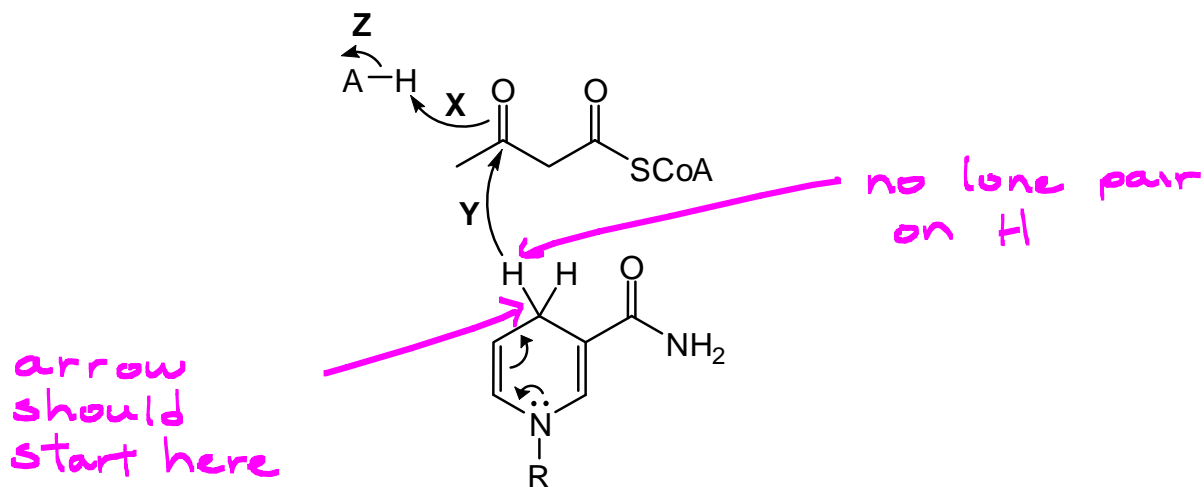


tautomerize twice

18. When glucose is metabolized into pyruvate, which atoms of glucose become CO_2 ?

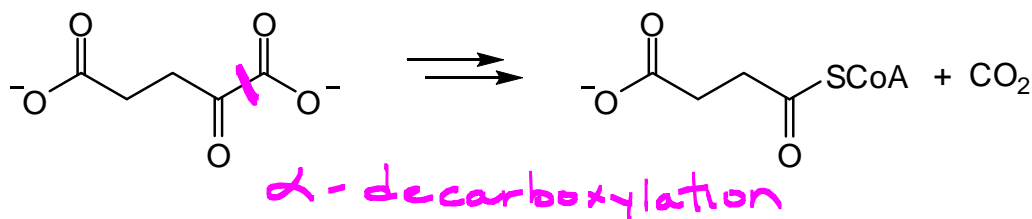
- A) All of them
- B) 1 and 6 only
- C) 1 and 4 only
- D) 1 only
- E) 3 and 4**

19. Below is a mechanism for the enzyme-catalyzed reduction of β -ketobutyryl-CoA by NADH? However, there is an error in the mechanism. What is the error?

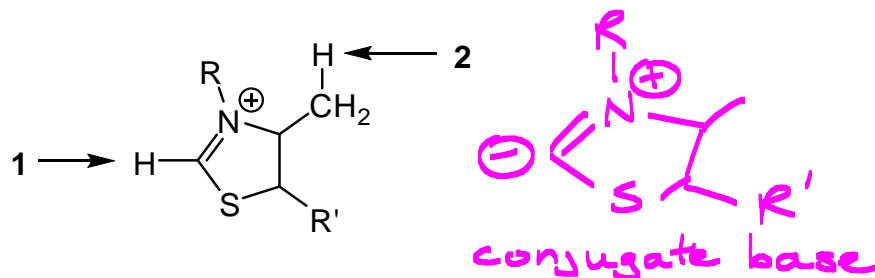


- A) The oxidized form of the nicotinamide ring is shown
- B) Arrow **X** is drawn in the wrong direction
- C) Arrow **X** should be a fishhook instead of a regular arrow
- D) Arrow Y** originates from the wrong place
- E) Arrows **X** and **Z** are in the wrong direction

20. α -Ketoglutarate dehydrogenase catalyzes the oxidative decarboxylation of α -ketoglutarate, as shown below. Which coenzyme is most likely required for the decarboxylation step of this reaction?

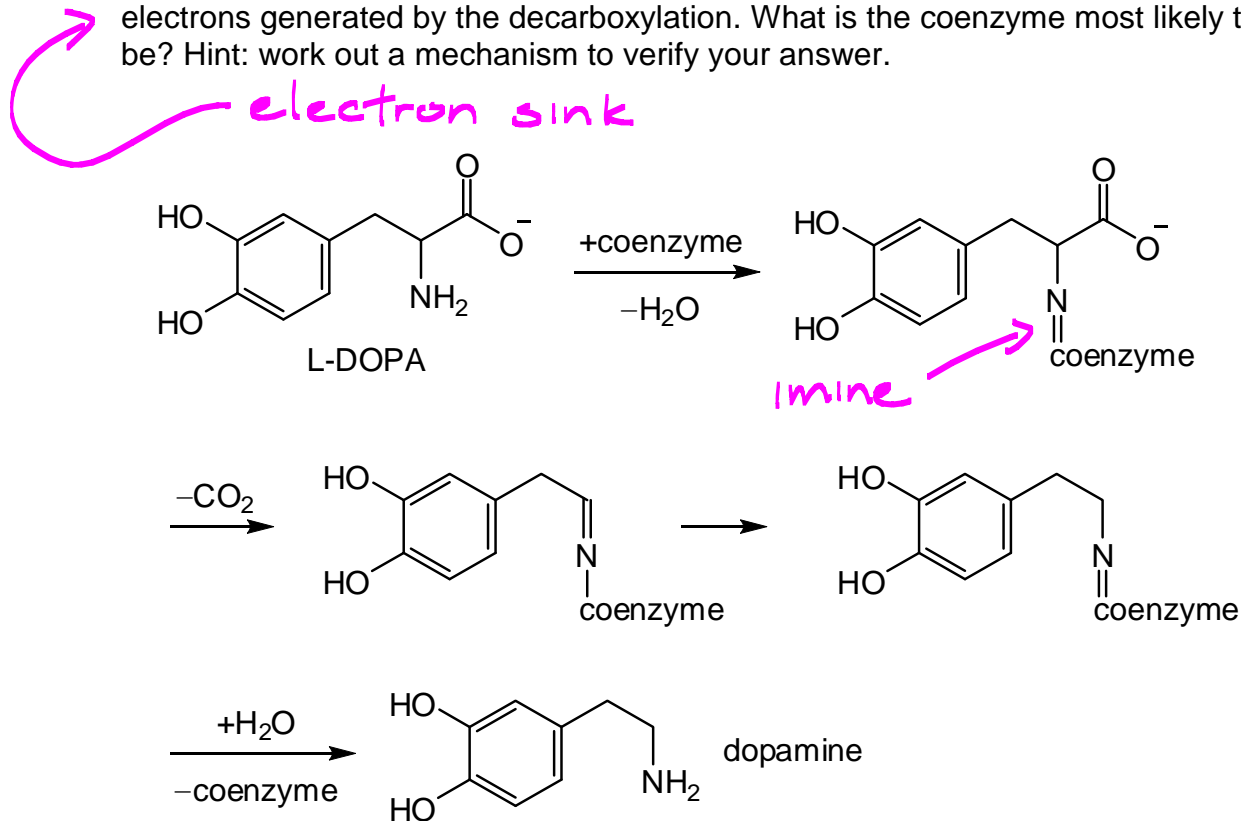


- A) Mg^{2+}
 B) Coenzyme-A
 C) FAD
 D) Ninhydrin
 E) Thiamine pyrophosphate
21. Which is the most acidic proton in thiamine pyrophosphate, and why?



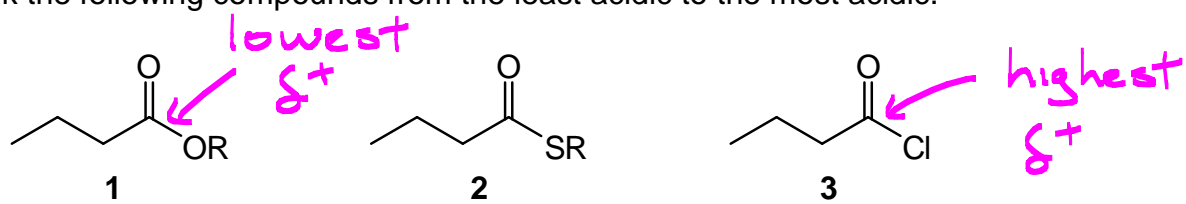
- A) Both **1** and **2** are of equal acidity because they are both bonded to carbon
 B) Proton **1**, because the conjugate base is stabilized a lone pair
 C) Proton **2**, because that's what we were told in class
 D) Proton **1**, because it has the highest pKa
 E) Proton **1**, because the conjugate base is stabilized by an inductively withdrawing group

22. *L-DOPA decarboxylase* is an enzyme targeted by many drugs used for the treatment of Parkinson's disease. The enzyme uses a coenzyme to catalyze the reaction sequence shown below. The coenzyme acts by temporarily storing the electrons generated by the decarboxylation. What is the coenzyme most likely to be? Hint: work out a mechanism to verify your answer.



- A) Thiamin pyrophosphate
 B) Pyridoxal phosphate
 C) Vitamin A
 D) Biotin
 E) NAD^+

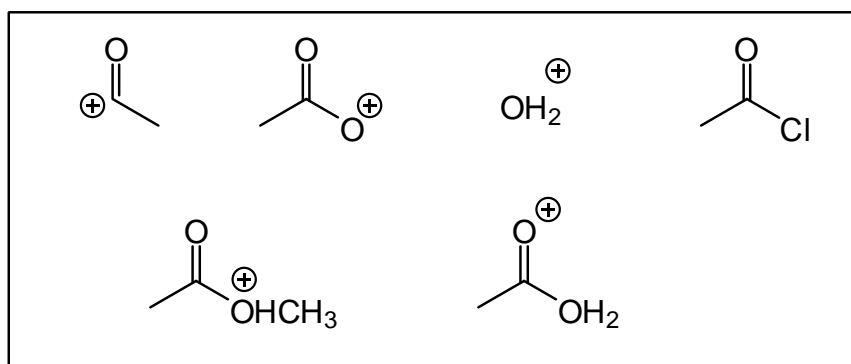
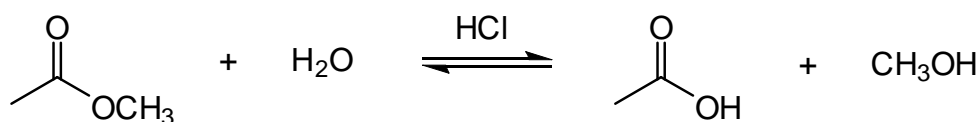
23. Rank the following compounds from the least acidic to the most acidic.



	Least	→	Most
A)	2		3
B)	1		3
C)	3		2
D)	3		1
E)	2		1

higher δ^+ makes α -H more acidic

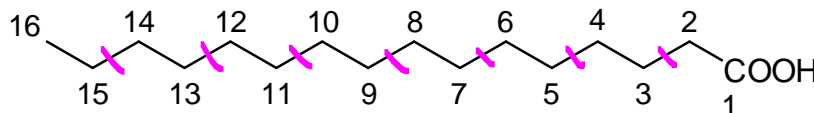
24. How many of the structures shown in the box are involved in the mechanism of the following reaction?



- A) 4 or more
 B) 2
 C) 1
 D) 3
E) None of them

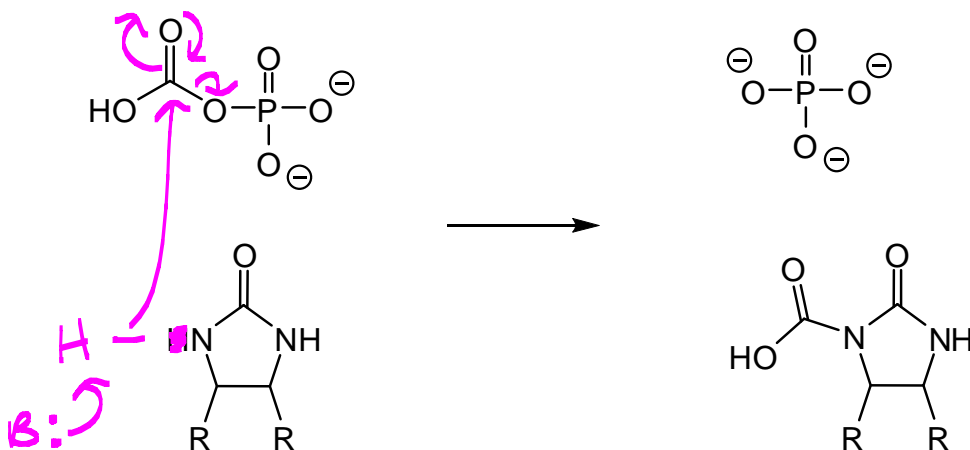
work out mechanism

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



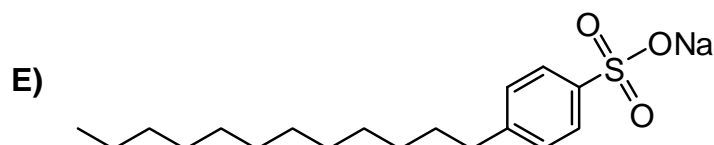
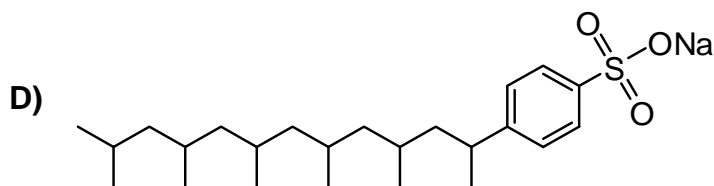
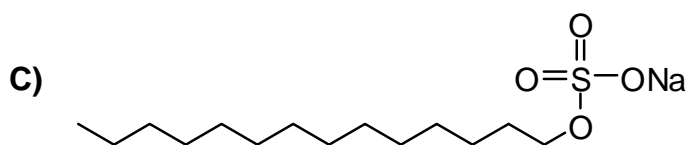
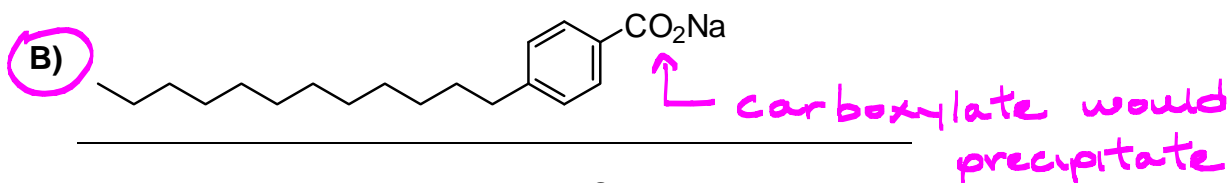
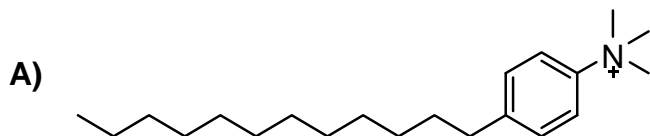
7 bonds made

- A) A double bond was reduced between C3 and C4. *5th*
- B) The bond between C6 and C7 was formed in the ~~third~~ Claisen reaction. *X*
- C) The ~~even~~ *odd*-numbered carbons were, at one time, attacked by NADPH. *X*
- D)** Seven equivalents of ATP were required to synthesis this fatty acid.
- E) Carbon 1 came from carbon dioxide.
26. Consider the reaction of biotin with carboxyphosphate to form carboxybiotin. Which statement(s) is/are correct?

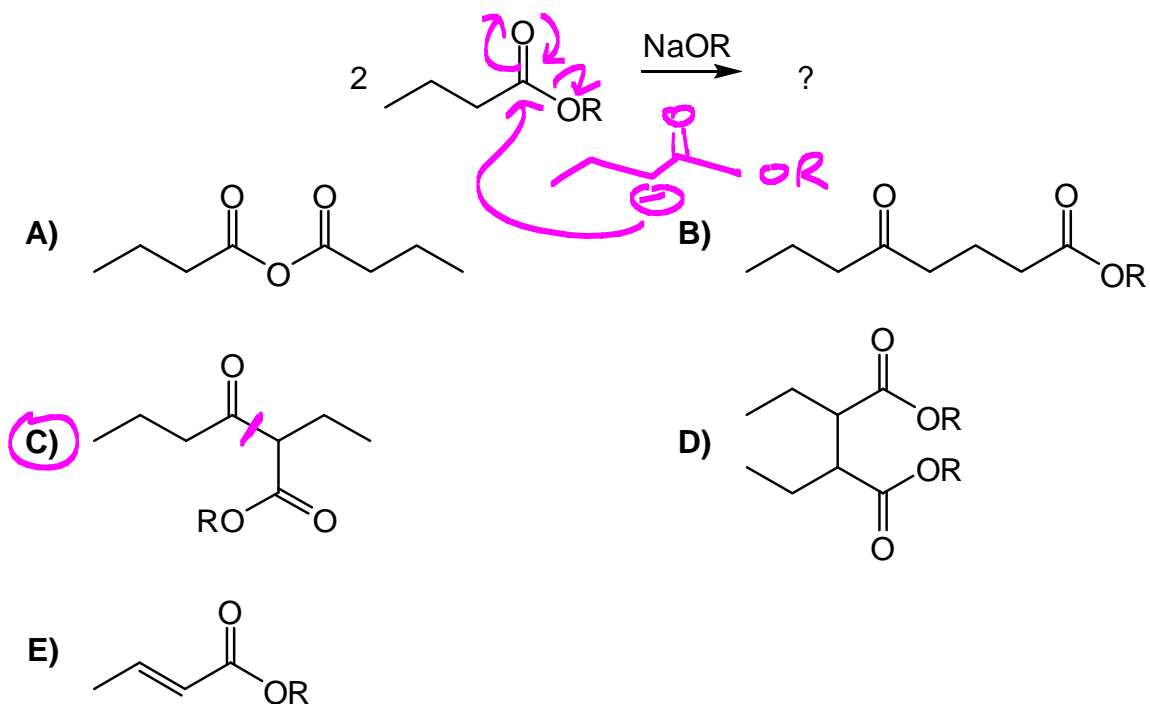


1. A carbon atom acts as an electrophile ✓
 2. Phosphate is the leaving group ✓
 3. A tetrahedral intermediate is formed during the reaction ✓
- A) 2 only
- B) 1 and 2 only
- C) 1 only
- D) 2 and 3 only
- E)** All statements are correct ✓

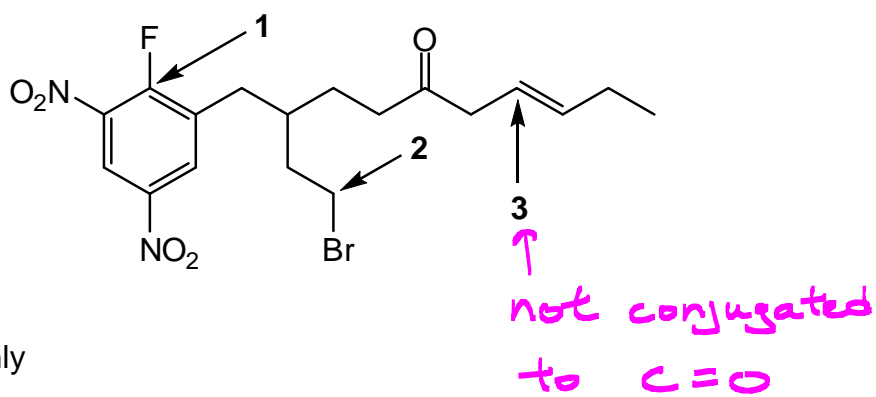
27. Which one of A – E is NOT a good cleaning agent in hard water?



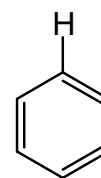
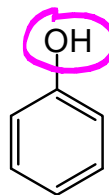
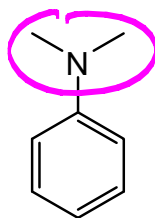
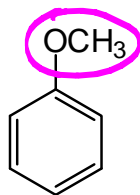
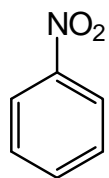
28. What is the product of the following Claisen condensation?



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



- (A) 1 and 2 only
 B) 2 and 3 only
 C) 1 only
 D) All of 1, 2, and 3
 E) 3 only

EDG
↓30. How many of the following aromatic compounds contain an *ortho/para* director?

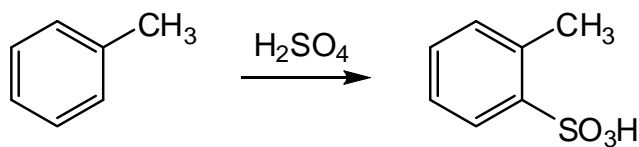
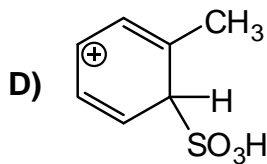
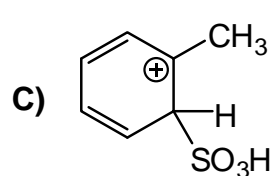
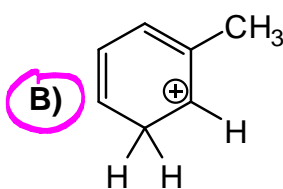
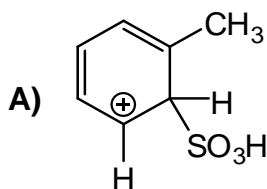
A) 2

B) 4

C) 5

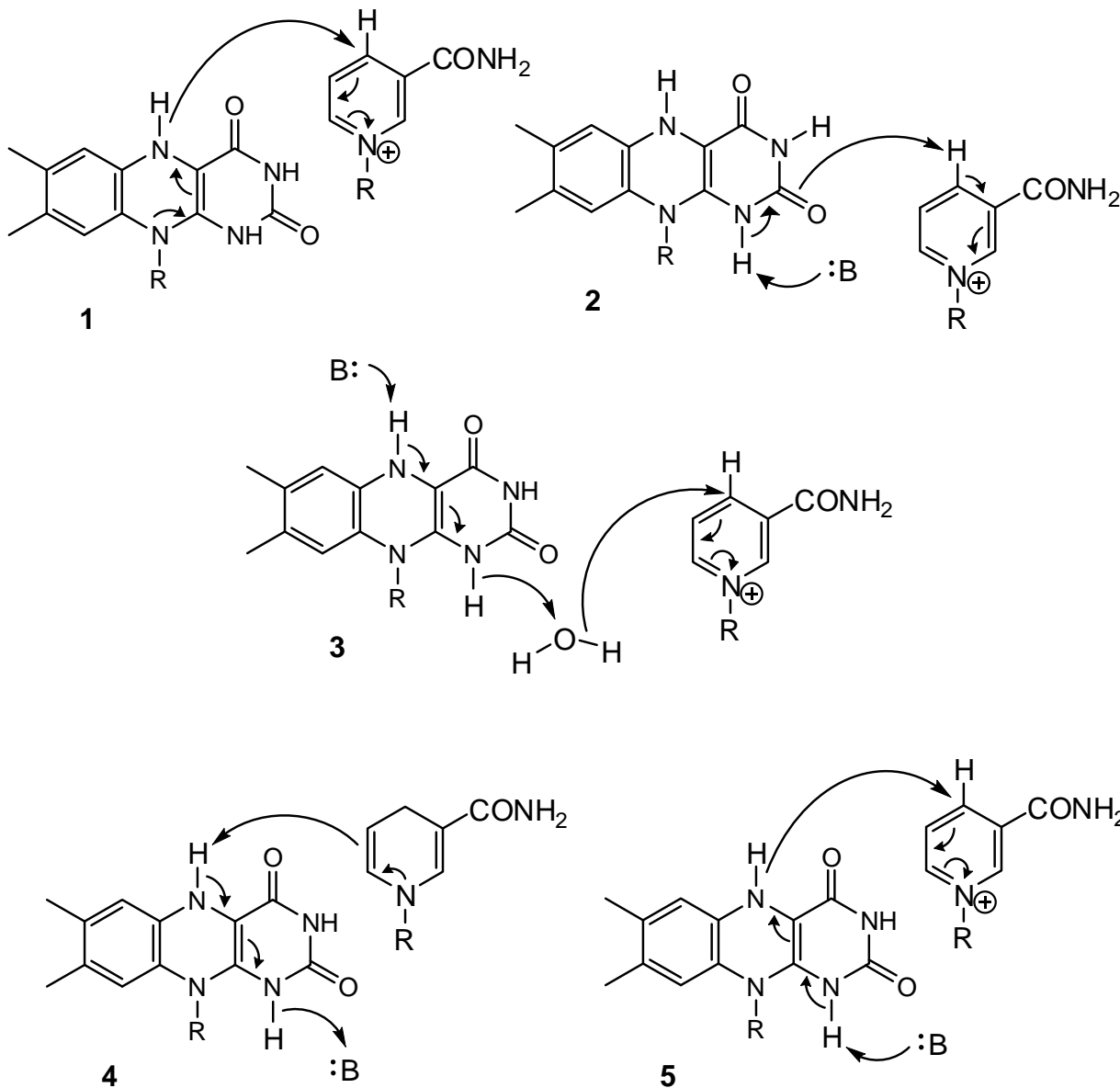
D) 3

E) 1

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

E) All are involved

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



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

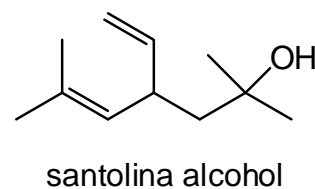
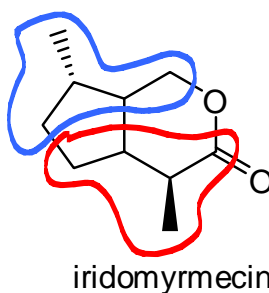
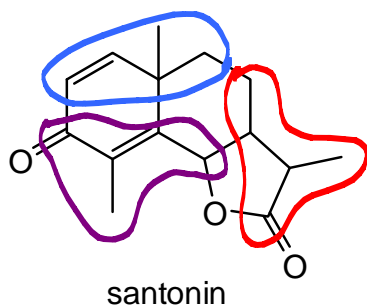
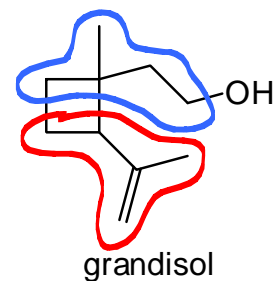
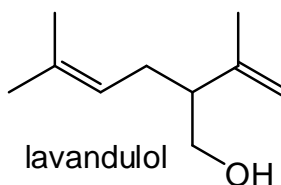
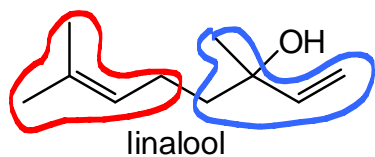
33. Organisms can change the composition of their cell membrane in response to changes in temperature. To prevent the membrane from “melting” when the temperature increases, how many of the following can occur?

want to increase melting point

- The fatty acid chains in the phospholipids become shorter **x**
- The fatty acids in the phospholipids isomerize from *trans* to *cis* **x**
- The fatty acid chains in the phospholipids become more unsaturated **x**
- A fatty acid chain is removed from each phospholipid to convert them into soaps or detergents **x**

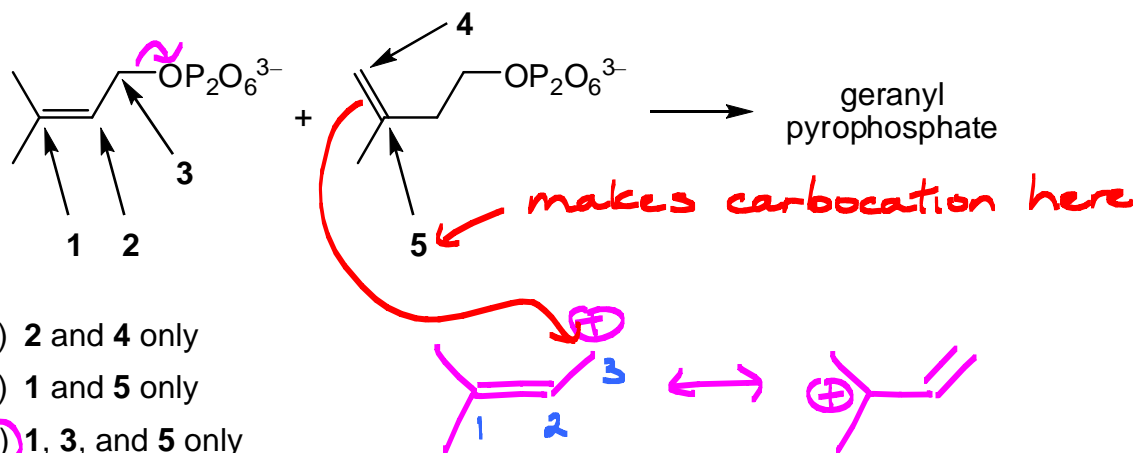
- A) 3
 B) 1
 C) 4
 D) 2
 E) None

34. Below is a selection of natural lipids. How many of them obey the isoprene rules?



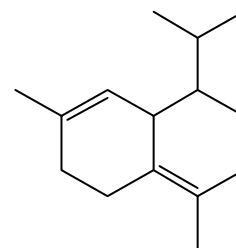
- A) 4
 B) 3
 C) 2
 D) 1
 E) 5

35. The enzyme-catalyzed reaction between dimethylallyl pyrophosphate and isopentenyl pyrophosphate to give geranyl pyrophosphate is shown below. Which of the following arrows indicate where there is a significant build-up of positive charge during the reaction? (Assume reaction proceeds S_N1)



- A) 2 and 4 only
 B) 1 and 5 only
 C) 1, 3, and 5 only
 D) 3 and 4 only
 E) 2, 3, and 5 only
36. How many moles of ATP and NAD(P)H are required to biosynthesize one mole of the terpene δ -cardinene, shown below, from acetyl-CoA?

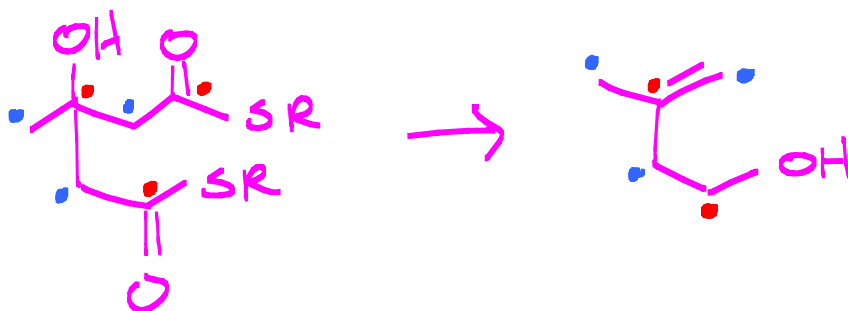
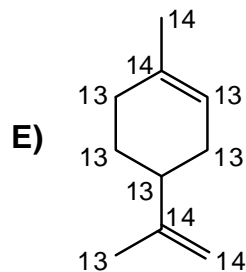
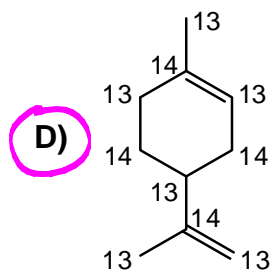
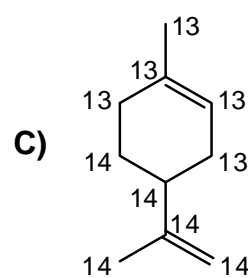
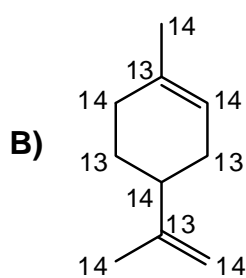
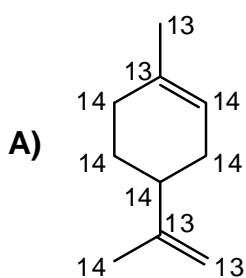
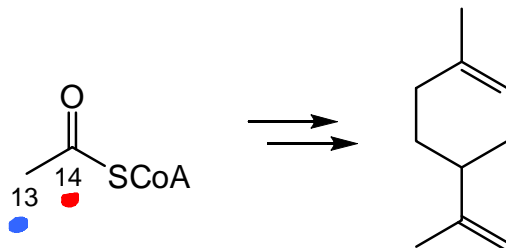
- A) 12 ATP and 6 NAD(P)H
 B) 9 ATP and 6 NAD(P)H
 C) 15 ATP and 15 NAD(P)H
 D) 15 ATP and 9 NAD(P)H
 E) 6 ATP and 12 NAD(P)H



C15 terpene

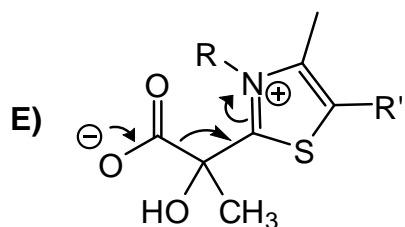
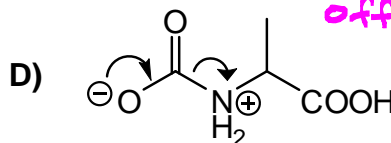
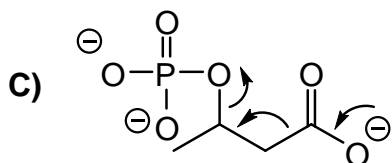
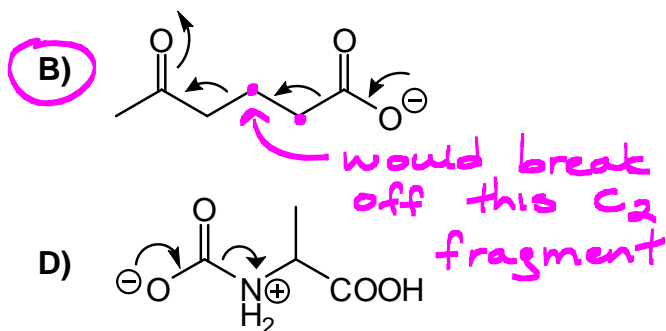
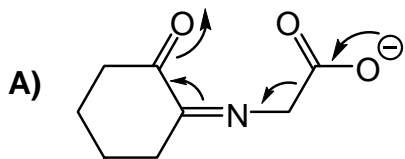
- each C_5 needs 3 acetyl-CoA,
 4 ATP (1 of which is used to
 make malonyl-CoA), and 2 NADPH

37. The compound below is the terpene limonene. It can be biosynthesized exclusively from acetyl-CoA that is labelled with ^{13}C and ^{14}C , as shown below. Which one of A – E shows the correct locations of the isotopes in the product?

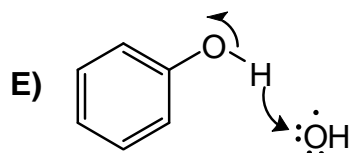
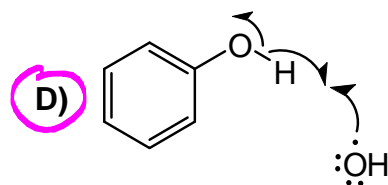
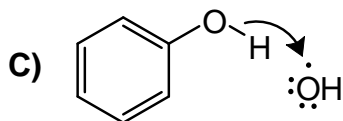
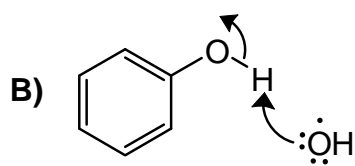
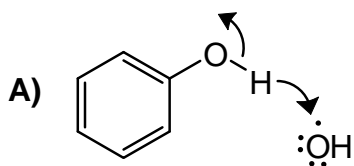


13 = head/back
14 = neck/tail

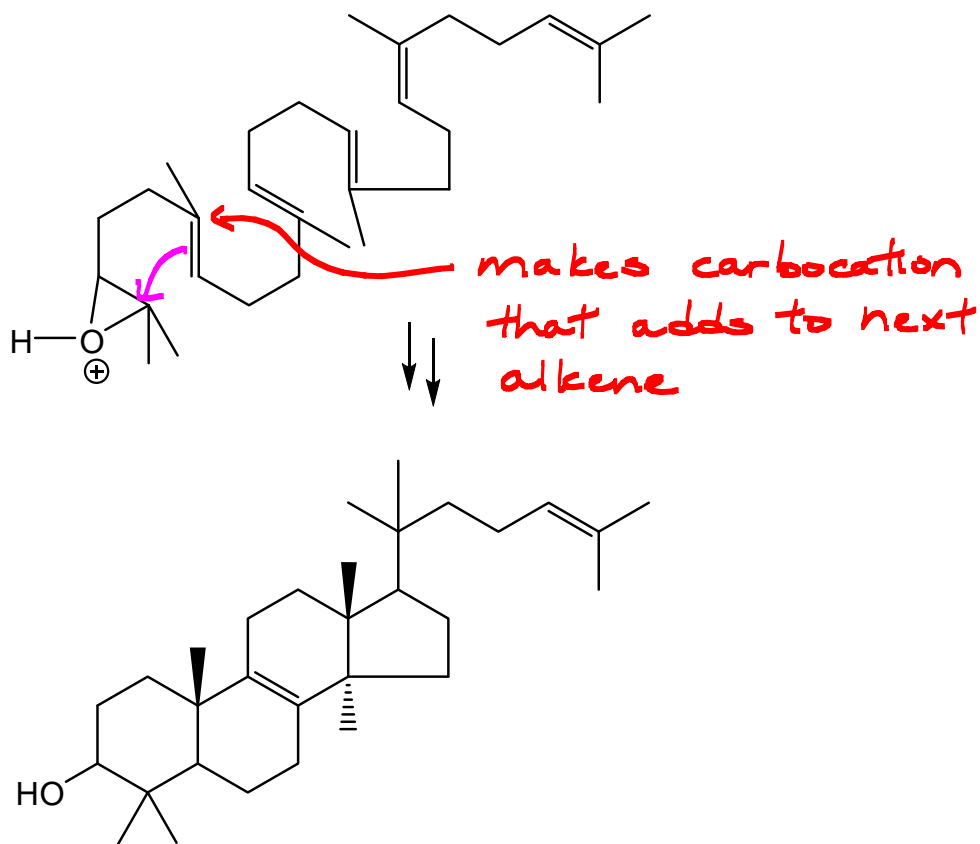
38. Which one of the following decarboxylation reactions is *least likely* to proceed according to the mechanism drawn?



39. Phenolic OH groups are particularly effective at scavenging free radicals, such as the hydroxyl radical. Which one of A – E correctly shows this reaction?

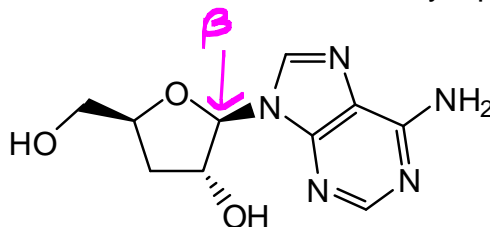


40. The conversion of protonated squalene epoxide to lanosterol involves steps that are mechanistically most similar to which one of A – E?



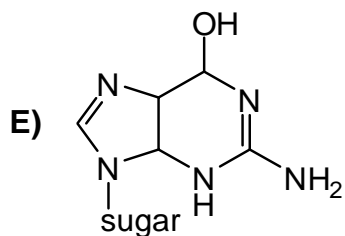
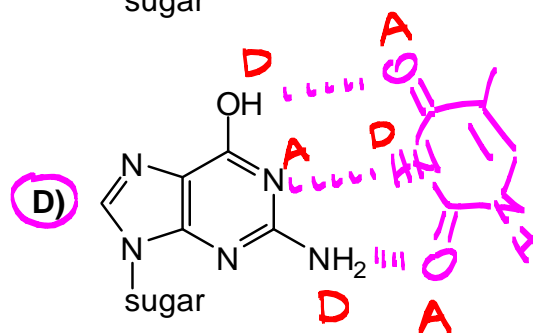
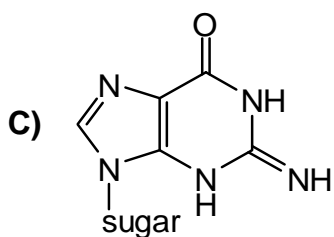
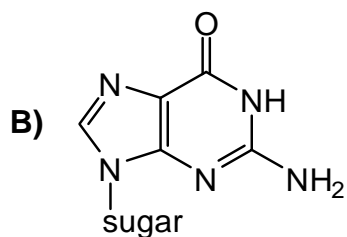
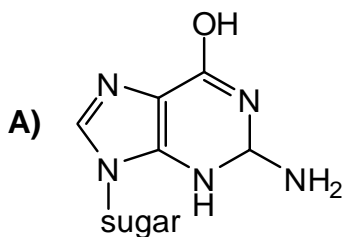
- A) Nucleophilic acyl substitution
- B) The acid-catalyzed polymerisation of propylene**
- C) Nucleophilic aromatic substitution
- D) Claisen condensation
- E) Michael addition

41. Cordycepin, shown below, has interesting properties as an anti-tumor, anti-fungal and anti-viral agent. Which statements about cordycepin are correct?



1. Cordycepin is a β -glycoside
 2. Cordycepin is a purine nucleoside analog
 3. Cordycepin is expected to act as a chain terminator in DNA synthesis because it lacks a 2'-OH *x lacks 3'-OH*
 4. The carbohydrate in cordycepin is D-3-deoxyarbinose *x ribose or xylose*
- A) 2 and 3 only
B) 1 and 3 only
C) 1, 2, and 4 only
D) 1 and 2 only
E) 2 and 4 only

42. A *tautomeric shift* is a type of DNA mutation caused by the tautomerism of a template nucleobase during DNA replication. For example, a GT base pair can form as a result of the tautomerism of G. Which one of the following is a tautomer of G that can most effectively form a base pair with T?

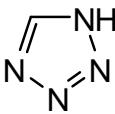
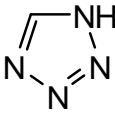
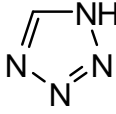
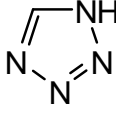
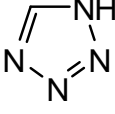


43. Which of the following statements is/are correct?

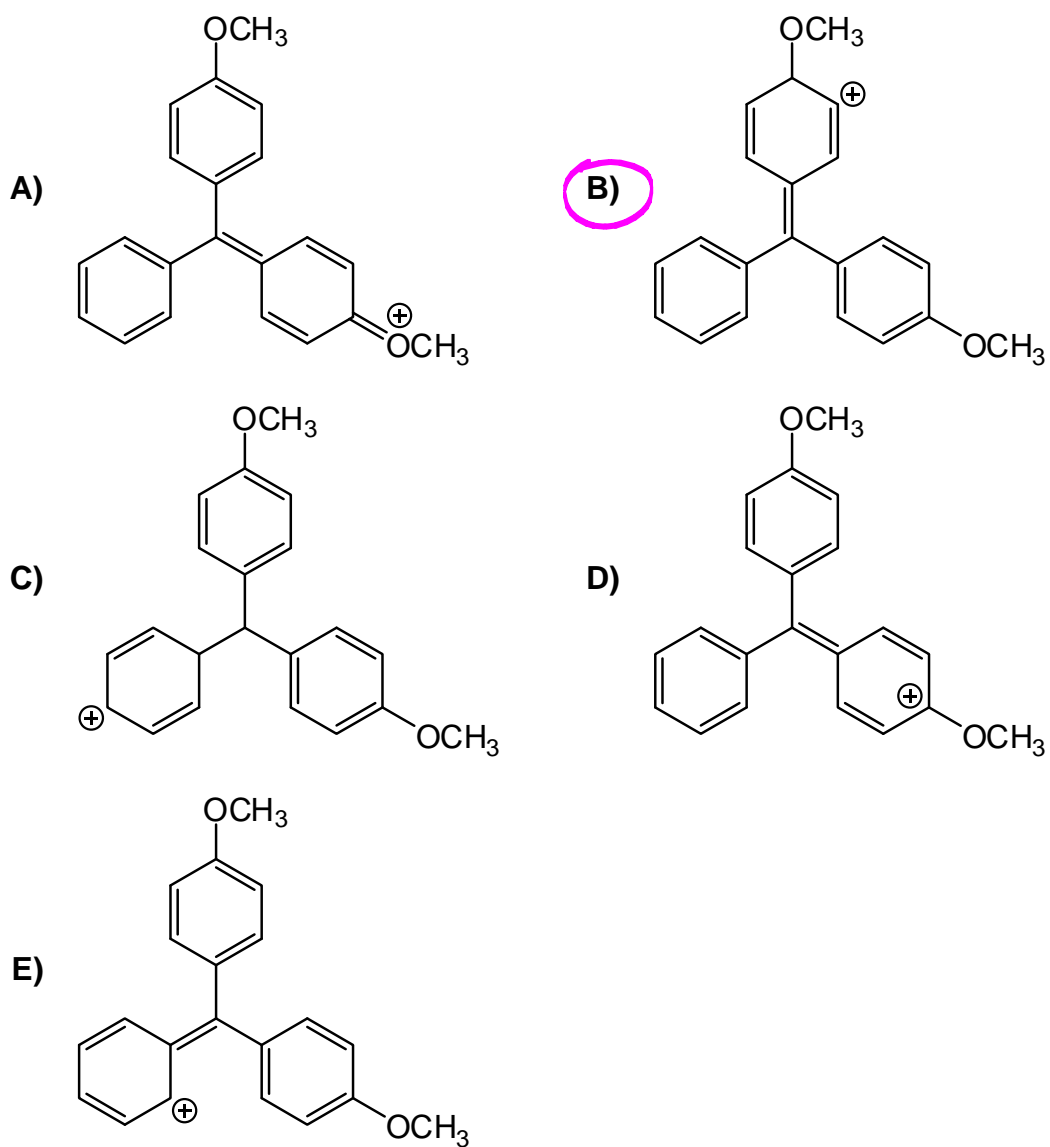
1. In dye-terminator sequencing, the dye terminators present in all four nucleotides must have the same wavelength of maximum fluorescence. ~~X~~ *must be different*
2. When separating DNA, the electrophoretic gel must be set up so that the loading wells are closest to the positive electrode. ~~X~~ *negative*
3. Pyrosequencing does not require thermocycling. ✓

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

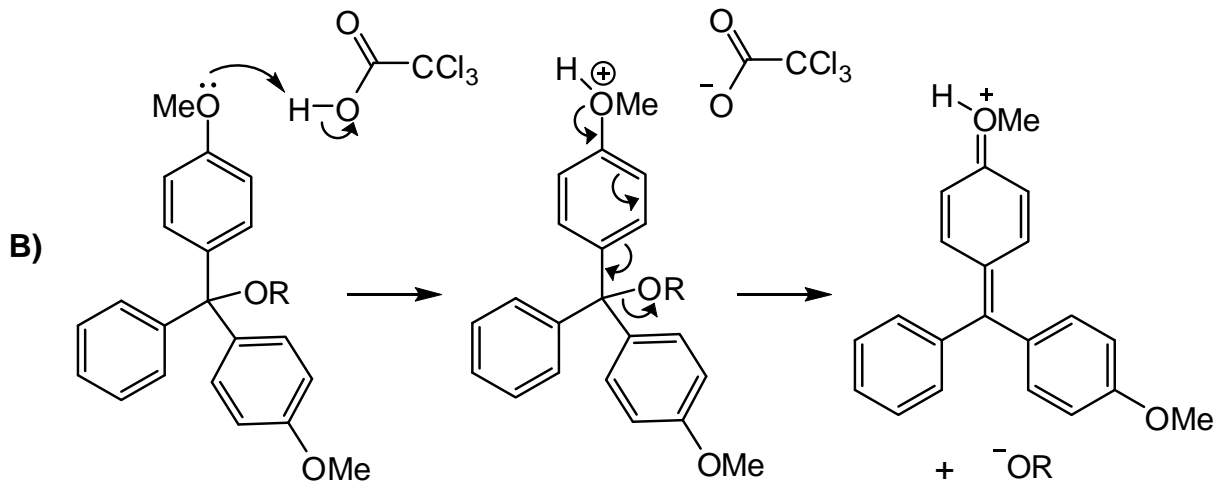
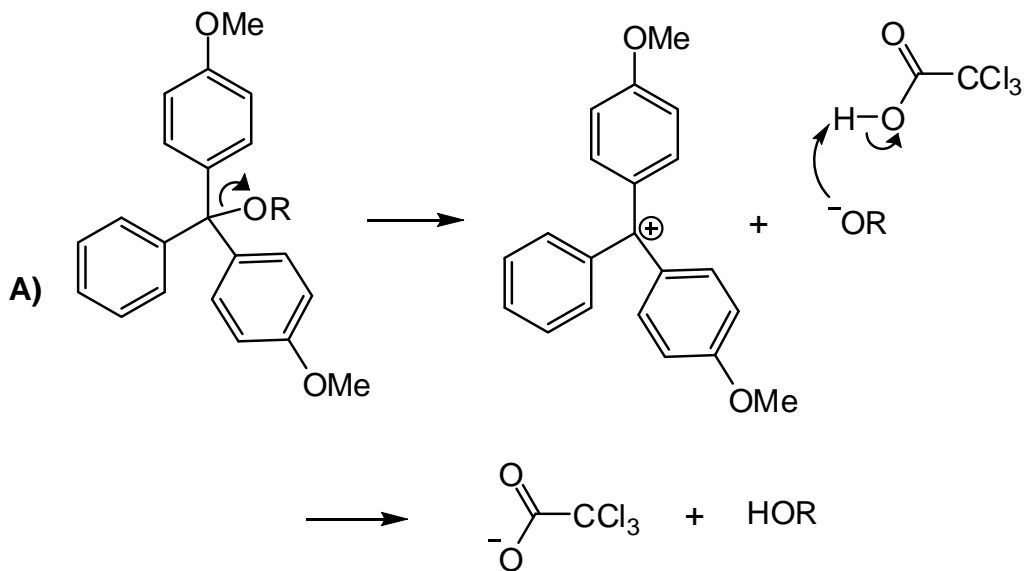
44. Rank the compounds in the order of increasing pKa, from lowest to highest.

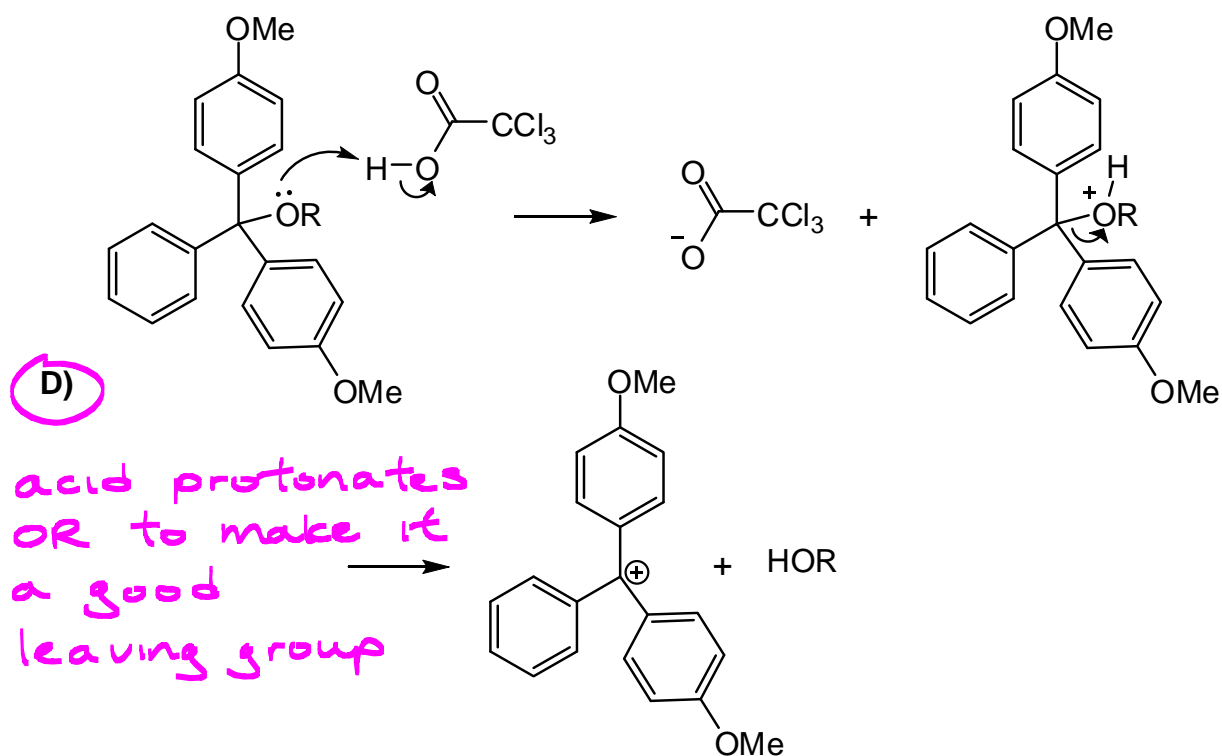
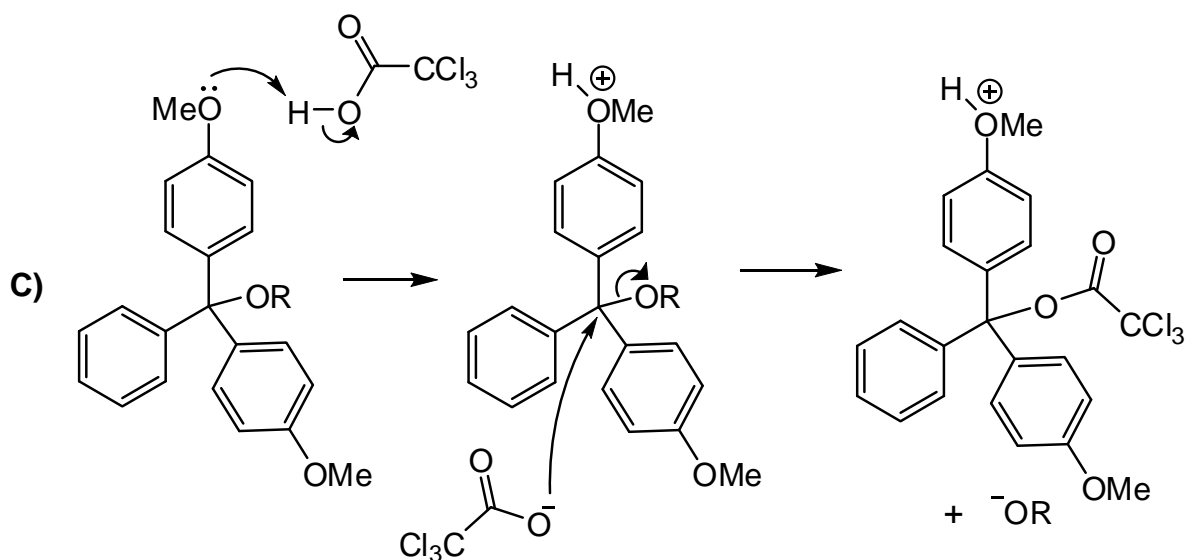
	Lowest pKa			Highest pKa
A)	HBr	F ₃ CCOOH	Cl ₃ CCOOH	
B)	HBr	Cl ₃ CCOOH	F ₃ CCOOH	
C)		Cl ₃ CCOOH	F ₃ CCOOH	HBr
D)		HBr	F ₃ CCOOH	Cl ₃ CCOOH
E)	HBr		F ₃ CCOOH	Cl ₃ CCOOH

45. Which one A – E is NOT a correct resonance structure of the dimethoxytrityl carbocation?



46. Which one of the following mechanisms most correctly describes the removal of the DMT protecting group using trichloroacetic acid? (Note: this question spans two pages.)





E) None of the above

47. How many of the following statements are correct?

- Polyaromatic hydrocarbons are metabolized to carcinogens ✓
- Toluene is more hazardous to human health than is benzene because toluene gets metabolized ✗
- UV-C light is longer wavelength than UV-B light ✗

shorter

A) 2

B) 1

C) Do not choose this answer

D) 3

E) None are correct

48. How many of the following statements about NADH are correct?

- Both phosphorous atoms are in the +5 oxidation state. ✓
- It contains two phosphate-ester linkages ✓
- It contains one phosphoric anhydride ✓
- It acts as a reducing agent by donating a hydride ion ✓

A) 3

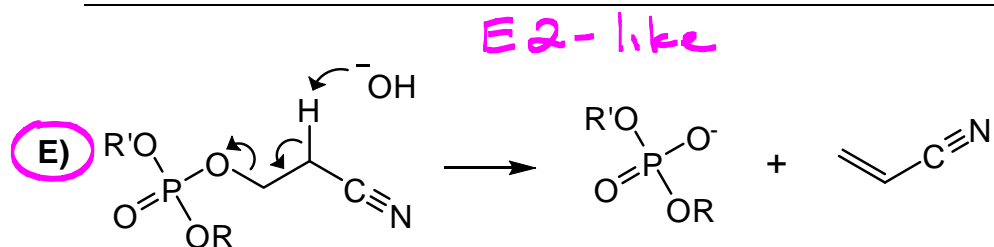
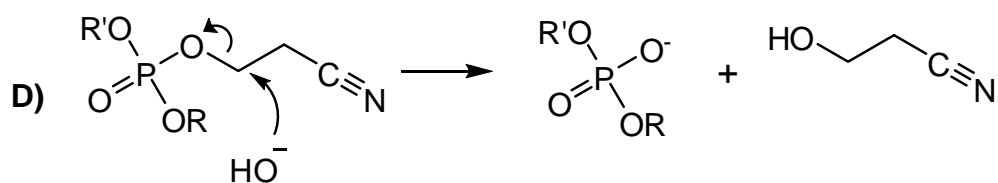
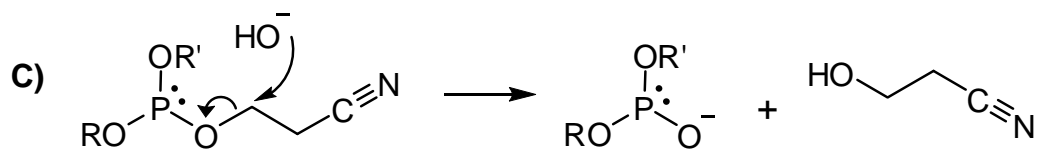
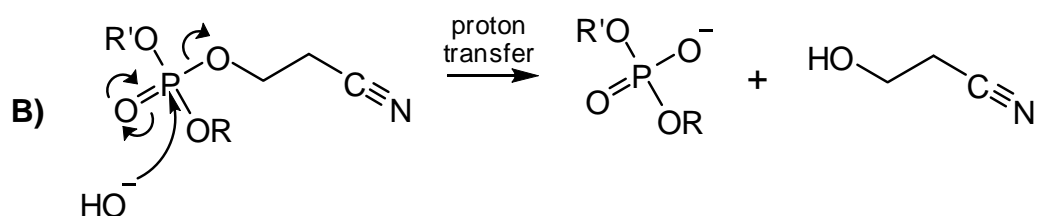
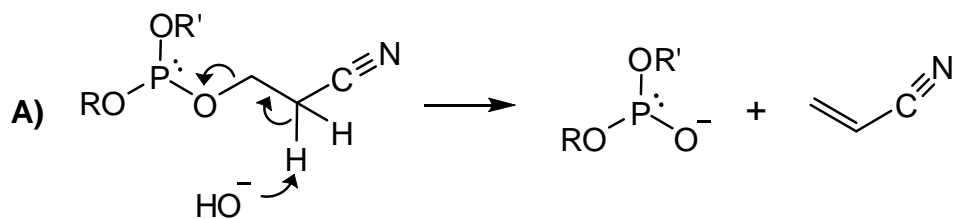
B) None are correct

C) 1

D) 2

E) All are correct

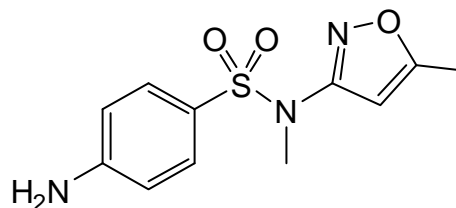
49. The cyanoethyl group protecting a phosphate can be removed by a β -elimination using a base such as hydroxide. What is the correct mechanism?



50. Which one of the following is NOT a common way to discover a new drug?

- A) Using combinatorial chemistry and high-throughput screening
- B) Extracting compounds from plant or animal sources
- C) Modifying the structure of known drugs
- D) Asking doctors to use drugs off-label
- E) Designing a drug by computational chemistry

51. *N*-Methylsulfamethoxazole, shown on the right, is a sulfanilamide-class drug but does not have any antibacterial activity. Why?

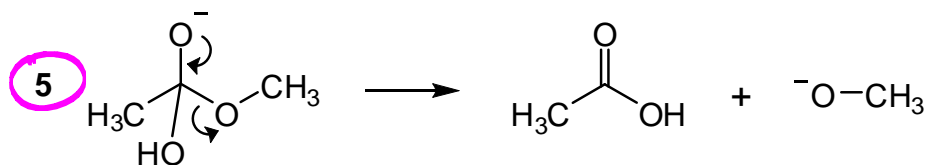
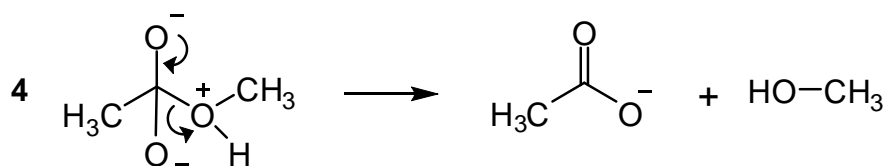
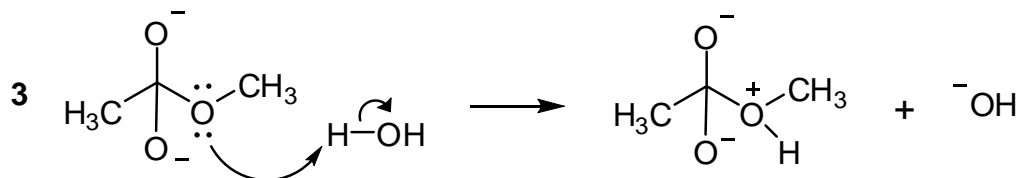
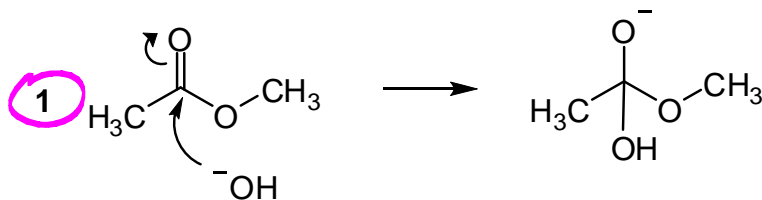


- A) The pKa of *N*-methylsulfamethoxazole is too low
- B) The compound is too nonpolar and sticks to the cell membrane
- C) The sulfonamide group cannot be deprotonated *no H on N*
- D) The amino group is always protonated and cannot cross the cell membrane
- E) The five-membered ring is sterically demanding and prevents the drug from binding to its target

52. Before a pharmaceutical drug can be marketed, the drug must be approved by the FDA. What does "FDA" stand for?

- A) Federal Drug Agents
- B) Florida District Attorney
- C) Federation of Drug Approvers
- D) Friends of Drugs Association
- E) Food and Drug Administration

53. Which step(s) is/are part of the accepted mechanism for the saponification of methyl acetate?



- A) 1 and 5 only
 B) 1, 2, 3, and 4 only
 C) 1 and 2 only
 D) 5 only
 E) None are part of the accepted mechanism

54. What is the precipitate formed when HCl is added to a solution of sodium stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$? *acid protonates RCOO^- , RCOOH is insoluble*
- A) Glycerol
 - B) $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_2\text{Na}$
 - C) Two equivalents of $\text{CH}_3(\text{CH}_2)_7\text{COOH}$
 - D) $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
 - E) NaCl
55. Why is the α -bromination of *meta*-chloropropiophenone termed an *autocatalytic* process?
- A) The thermal energy in the reactants automatically catalyzes the reaction
 - B) The byproduct formed in the reaction acts as a catalyst
 - C) *meta*-Chloropropiophenone catalyzes the bromination reaction
 - D) All reactions that occur at the α carbon are termed autocatalytic
 - E) Br_2 catalyzes the bromination reaction