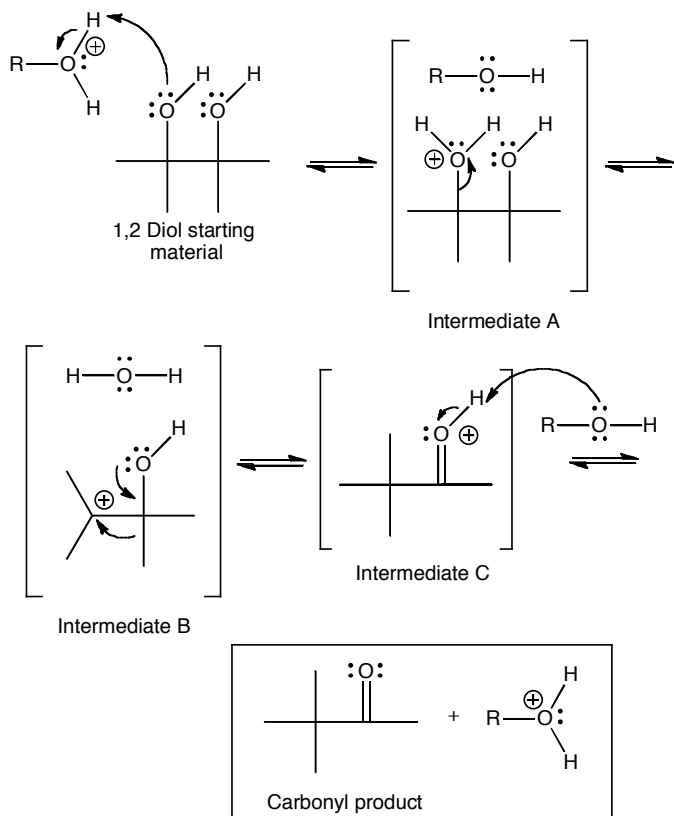


**Directions.** Most questions in the Physical Sciences test are organized into groups, each preceded by a descriptive passage. After studying the passage, select the one best answer to each question in the group. Some questions are not based on a descriptive passage and are also independent of each other. You must also select the one best answer to these questions. If you are not certain of an answer, eliminate the alternatives that you know to be incorrect and then select an answer from the remaining alternatives. Indicate your selection by blackening the corresponding oval on your answer document. A periodic table is provided for your use. You may consult it whenever you wish.

### Passage I (Questions 1 – 4)

The pinacol rearrangement occurs when a 1,2 diol is exposed to acidic conditions. The reaction begins when one of the -OH groups is protonated. Following departure of water, a carbocation is formed. The interesting part of this reaction is that an adjacent alkyl group or H atom migrates to the carbocation center to create a more stable cation. Loss of a proton gives the carbonyl product.



When the starting diol is not symmetric, the initial carbocation forms on the side that makes the more stable carbocation.

1. Which of the intermediates in this reaction are stabilized by resonance delocalization?

- A. Intermediate A only
- B. Intermediate B only
- C. Intermediate C only
- D. Intermediate B and C

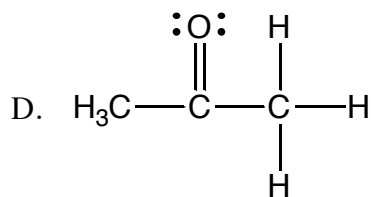
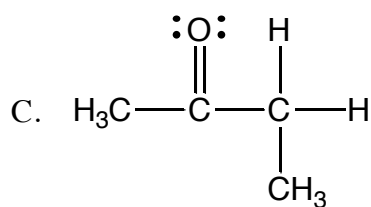
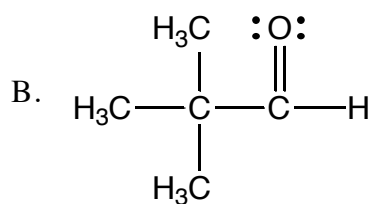
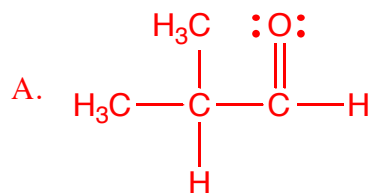
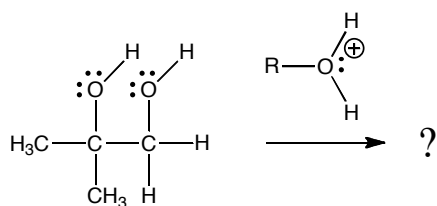
2. The reaction occurs in acidic solution. Which statement best describes the role of acid in this reaction.

- A. The acid is acting in a catalytic fashion
- B. Acid is not involved in this reaction.
- C. The reaction uses one equivalent of acid.
- D. The reaction produces one equivalent of acid.

3. Based upon your answer to question 2, identify the correct statement

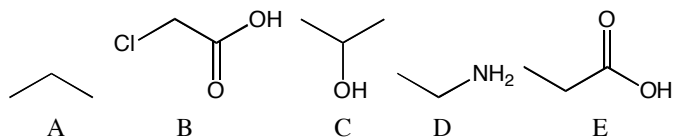
- A. The pH of the reaction will drop over time.
- B. The pH of the solution will rise over time.
- C. The pH of the solution will rise at first, then drop.
- D. The pH of the solution will stay the same.

4. The following 1,2 diol undergoes the pinacol rearrangement. Predict the structure of the product.



Questions 5 through 9 are NOT based on a descriptive passage.

5. List the following molecules in terms of relative acid strength rank order, such that the first molecule listed is the strongest acid and the last is the weakest acid.



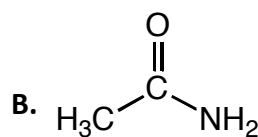
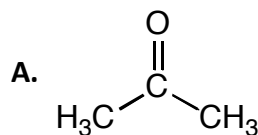
A. B, E, D, C, A

B. B, E, C, D, A

C. E, B, C, D, A

D. A, D, C, E, B

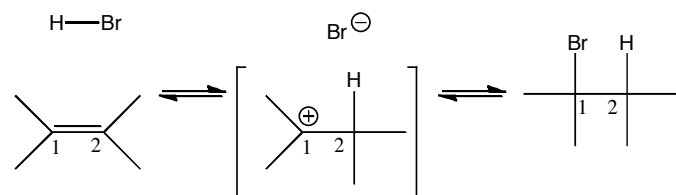
6. Three of the following molecules have a permanent dipole moment and one does not. Indicate which is the molecule without a permanent dipole moment.



C.  $\text{CCl}_4$

D.  $\text{CHCl}_3$

7. In the following abbreviated mechanism, the atoms are numbered so you can keep track of them.



For the atom labeled as 1, what is its hybridization during this sequence of steps?

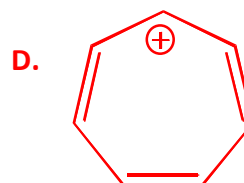
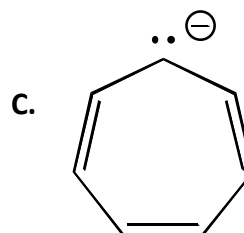
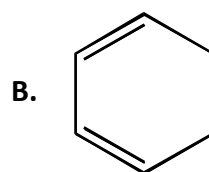
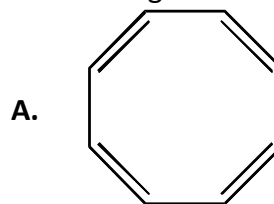
A.  $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{sp}^2$

B.  $\text{sp}^2$ ,  $\text{sp}^3$ ,  $\text{sp}^3$

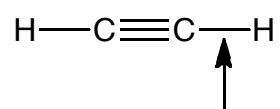
C.  $\text{sp}^2$ ,  $\text{sp}^2$ ,  $\text{sp}^3$

D.  $\text{sp}^2$ ,  $\text{sp}$ ,  $\text{sp}^2$

8. One of the following molecules displays the properties associated with being aromatic. Which of the following is the aromatic one?



9. Describe the bond indicated by the arrows in terms of overlap of hybridized orbitals.



A.  $\pi_{\text{C}_{\text{sp}}-\text{H}_{1\text{s}}}$

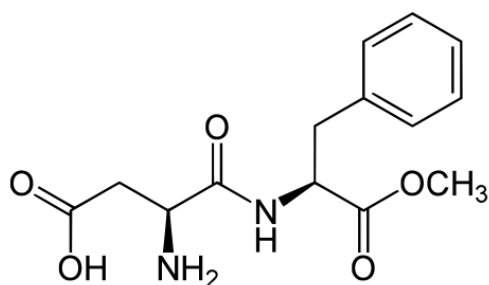
B.  $\sigma_{\text{C}_{\text{sp}^3}-\text{H}_{2\text{p}}}$

C.  $\sigma_{\text{C}_{\text{sp}}-\text{H}_{1\text{s}}}$

D.  $\sigma_{\text{C}_{\text{sp}^2}-\text{H}_{1\text{s}}}$

## Passage II (Questions 10-14)

The following molecule is Nutrasweet™, also known as Aspartame, an artificial sweetener. Although sweet to the taste, this molecule is not a carbohydrate. Scientists still disagree about what parameters make a molecule taste sweet to human beings. Nutrasweet™ is 200 times sweeter than sucrose, namely common table sugar.



The above structure was copied from a Wikipedia article. More about that in question 14.

Several attempts have been made to declare Nutrasweet™ dangerous. A common concern is that under prolonged exposure to strongly acidic conditions, especially when accompanied by heating, methanol can be produced from the Nutrasweet™ molecule. Methanol is a toxic substance when consumed in large amounts, but there is not definitive evidence that the small amount present in Nutrasweet™ is harmful.

Because of its commercial value, Nutrasweet™ has been synthesized in a number of ways. One of the most successful involves protecting the amino group of L-aspartic acid followed by converting its two acid groups into the anhydride. The methylated form of L-Phenylalanine is then reacted with the anhydride. Removal of the amine protecting group completes the synthesis.

10. How many amide groups are in Nutrasweet™?

- A. 1
- B. 2
- C. 3
- D. 4

11. Nutrasweet™ has two chiral centers. Write the correct designation for the two chiral centers, listed as the leftmost one first, followed by the rightmost one.

- A. R,R
- B. R,S
- C. S,R
- D. S,S

12. Identify the reaction under acidic conditions that leads to the production of methanol

- A. Amide hydrolysis
- B. Ester hydrolysis
- C. Acetal hydrolysis
- D. Lactonization

**13.** The  $pK_a$  value for an ammonium ion is around 10, and the  $pK_a$  value for a carboxylic acid is around 3. Using this information, predict the protonation state of Nutrasweet™ when the pH is neutral, 7.0

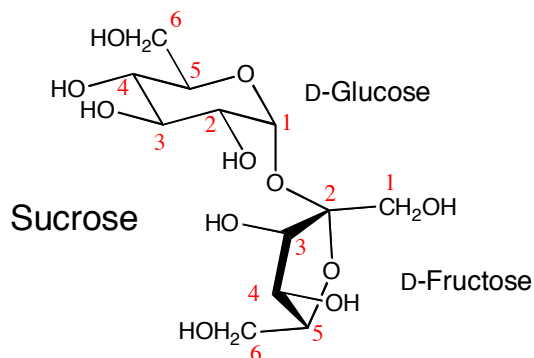
- A.** The carboxylic acid is deprotonated and negatively charged and the amine group is not protonated and neutral.
- B.** The carboxylic acid is protonated and neutral and the amine group is protonated and positively charged.
- C.** The carboxylic acid is deprotonated and negatively charged and the amine group is protonated and positively charged.
- D.** The carboxylic acid is protonated and neutral and the amine group is protonated and positively charged.

**14.** Remembering that the structure of Nutrasweet™ in the passage came from a Wikipedia article, what pH value would explain the protonation state of Nutrasweet™ indicated by the structure?

- A.** pH 2.0, near the pH of actual carbonated soft drinks.
- B.** pH 7.0, neutral pH
- C.** pH 10.0, basic pH
- D.** There is no pH that would produce the protonation state of the molecule shown.

### Passage III (Questions 15-18)

Continuing with the sweetness theme, table sugar is a disaccharide formed from the two carbohydrates D-glucose and D-fructose as shown below.



Sucrose is produced in large quantities by both sugar cane and sugar beets. Although easy to grow, these crops require significant processing in large plants to create pure sugar. As a result, sugar produced this way is relatively expensive.

In an effort to reduce the price of making foods sweet, the food additive industry turned to nature for inspiration. Honey is a complex substance, but by far the major components are the monosaccharides D-fructose and D-glucose, the two monomers found in the disaccharide Sucrose. In natural honey, the ratio of D-fructose : D-glucose is approximately 1:1, with the fructose often being in slight excess. High fructose corn syrups are composed of D-fructose and D-glucose in various ratios, intended to mimic natural honeys. For example, the formulation used most often in soft drinks is HFCS 55, is 55% D-fructose, 42% D-glucose. High fructose corn syrup is produced by converting the relatively inexpensive starch from corn into D-glucose, then turning some of this D-glucose into D-fructose. The large scale of corn production in the industrialized world, combined with the efficiency of this process, enables high fructose corn syrup to be considerably less expensive than sucrose.

There have been claims that high fructose corn syrup directly leads to obesity more than sucrose.

Detailed study has failed to establish any direct link between high fructose corn syrup consumption and obesity, although most experts agree the low cost of high fructose corn syrup has contributed to higher consumption, which can be blamed as an indirect cause of increased obesity. Of course, a healthy lifestyle including regular exercise will insure proper weight control over your entire life!

15. D-Glucose and D-fructose can be described as the following:

- A. Hexose, hexose, respectively
- B. Hexose, pentose, respectively
- C. Pentose, hexose, respectively
- D. Pentose, pentose, respectively

16. D-Glucose and D-fructose can be described as the following:

- A. Pyranose, pyranose, respectively
- B. Pyranose, furanose, respectively
- C. Furanose, pyranose, respectively
- D. Furanose, furanose, respectively

17. D-Glucose and D-fructose can be described as the following:

- A. Aldose, aldose, respectively
- B. Aldose, ketose, respectively
- C. Ketose, aldose, respectively
- D. Ketose, ketose, respectively

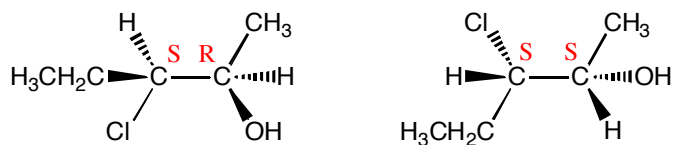


**18.** The bond between D-glucose and D-fructose is referred to as the following kind of bond:

- A.**  $\alpha$ -1,4-glycosidic bond
- B.**  $\alpha$ -1,2-glycosidic bond
- C.**  $\beta$ -1,4-glycosidic bond
- D.**  $\beta$ -1,2-glycosidic bond

Questions 19 through 22 are NOT based on a descriptive passage.

19. What is the relationship between the following two molecules

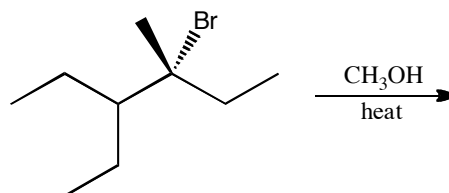


- A. Constitutional isomers
- B. Enantiomers
- C. Diastereomers
- D. The same molecule

20. Predict the predominant product(s) of the reaction between R-2-bromobutane with sodium cyanide.

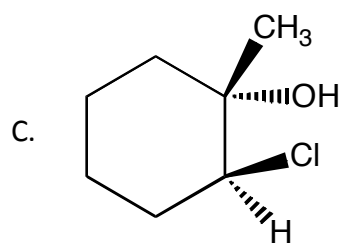
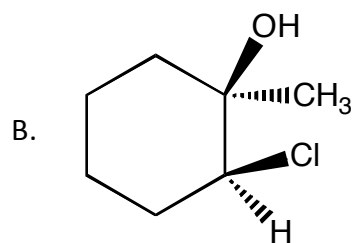
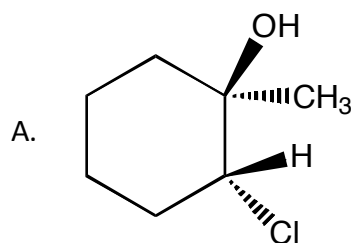
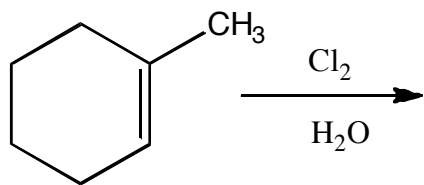
- A.
- B.
- C.
- D. All of the above

21. Predict the predominant product(s) of the following reaction:



- A.
- B.
- C.
- D. All of the above

22. Predict the predominant product(s) of the following reaction:



D. Products A. and C. as a racemic mixture

### Passage IV (Questions 23-25)

The valence shell electron pair repulsion (VSEPR) model is presented to organic chemistry students to help them predict the shapes of molecules. The idea behind VSEPR is that areas of electron density repel each other so that the geometry of bonds and/or lone pairs of electrons around any one atom places these areas as far apart as possible. For four areas of electron density, that means a tetrahedral geometry, for three areas of electron density that means a trigonal planar geometry and for two areas of electron density that means a linear geometry.

VSEPR is only a model, not a theory, and there are several important cases in which it gives a misleading prediction. Interestingly, there are several important situations critical to biology in which VSEPR breaks down. Two examples are shown here.

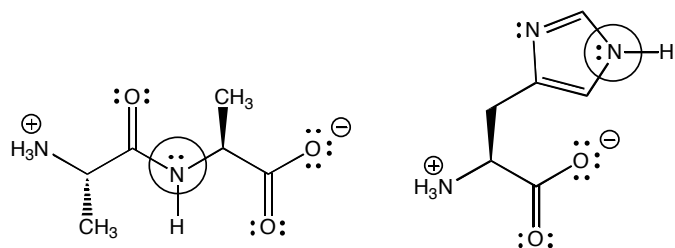


Figure 1

The N atoms indicated by the circle would be predicted by VSEPR to be tetrahedral in geometry because they each appear to have four areas of electron density surrounding them. However, in both cases, structural analysis has revealed that the atoms actually have a trigonal planar geometry.

23. What is the hybridization states of the circled atoms and what kind of orbital contains the lone pairs identified in the circles?

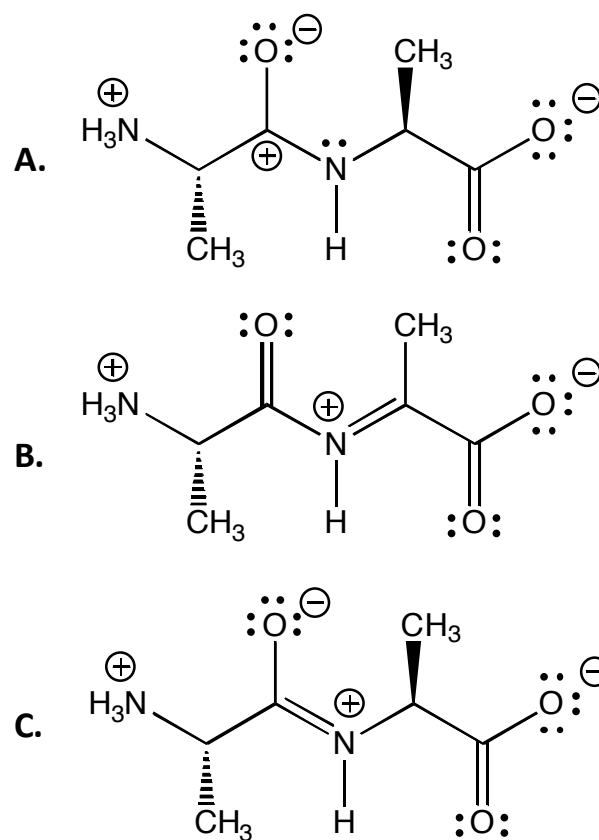
- A.  $sp$ ,  $2p$
- B.  $sp^2$ ,  $sp^2$
- C.  $sp^3$ ,  $2p$
- D.  $sp^2$ ,  $2p$

24. The molecule on the right in Figure 1 above is the amino acid histidine, and the five-membered ring is aromatic. Indicate which statements must therefore also be true

- A. There are a total of 6 electrons in the pi system, including the lone pair that is on the ring N atom that is not in the circle.
- B. There are a total of 6 electrons in the pi system, including the lone pair that is on the ring N atom inside the circle.
- C. The lone pair on the ring N atom not in the circle resides in an  $sp^2$  orbital on an  $sp^2$  hybridized N atom.

D. Both B and C

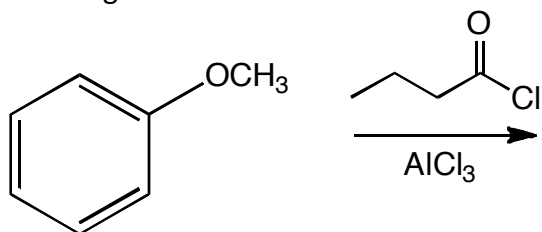
25. Which of the following are reasonable contributing structures for the amide bond of the molecule on the left in Figure 1.



D. Both A and C

Questions 26 through 29 are NOT based on a descriptive passage.

26. What is the predominant product(s) of the following reaction:



- A. and
- B.
- C. and
- D. and

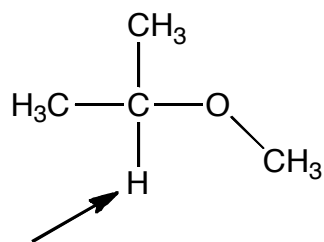
27. Ethyl propanoate is treated with one half an equivalent of sodium ethoxide,. Following reaction, the chemist opens the flask and adds enough acid to bring the pH down to below 2. What is the predominant product of this process?

- A.
- B.
- C. Racemic
- D. Racemic

28. In the medical imaging technique of MRI, what gives rise to the highest signal?

- A. Bone, teeth and finger nails
- B. Bone and teeth
- C. Water and fat
- D. Protein

29. In a  $^1\text{H}$ -NMR spectrum of the following molecule, how many peaks would be seen for the signal coming from the H atom indicated by the arrow?



- A. 7
- B. 10
- C. 4
- D. 1