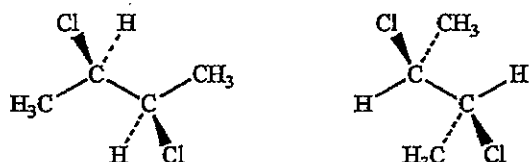


※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

### Multiple Choice Questions (2 points each, the total is 30 points)

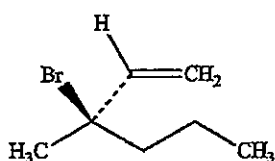
- A neutral oxygen has how many valence electrons?  
a. 4      b. 5      c. 6      d. 7
- Spreading of positive or negative charge over two or more atoms in a compound is called \_\_\_\_\_.  
a. isomerism  
b. delocalization  
c. stereoisomerism  
d. localization
- Which statement about orbitals is false?  
a. Orbitals are regions of space where electrons are found.  
b. Orbitals may contain up to two electrons each.  
c. Orbitals of equivalent energy are half filled before adding two electrons to any one of them.  
d. Orbitals are filled in order of decreasing energy.
- What are the correct orbital hybridizations for carbon in the following species?  
 $\text{CH}_3^+$        $\text{CH}_4$        $\text{CH}_3^-$   
a.  $\text{CH}_3^+$  is sp-hybridized  
b.  $\text{CH}_3^-$  is  $\text{sp}^2$ -hybridized  
c.  $\text{CH}_4$  is  $\text{sp}^2$ -hybridized  
d.  $\text{CH}_3^-$  is  $\text{sp}^3$ -hybridized
- (-)-cholesterol  
a. does not have a chiral center.  
b. is dextrorotatory.  
c. rotates the plane of polarized light counterclockwise.  
d. does not rotate polarized light.
- Which of the following is the definition of a pair of diastereomers?  
a. A pair of structures that are superimposable mirror images of one another  
b. A pair of stereoisomers that are non-superimposable mirror images of one another  
c. A pair of stereoisomers that are not mirror images of one another  
d. A pair of stereoisomers that have equal specific rotations

7. What is the relationship between the following pair of structures?



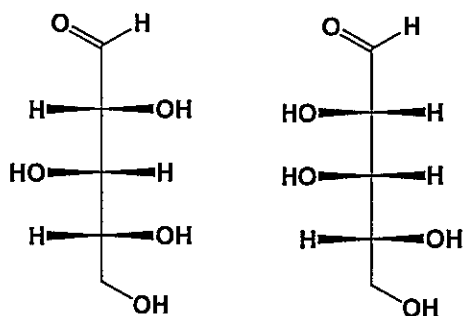
- They are enantiomers
- They are diastereomers
- The are constitutional isomers
- They are identical

8. What is the IUPAC name of the following compound?



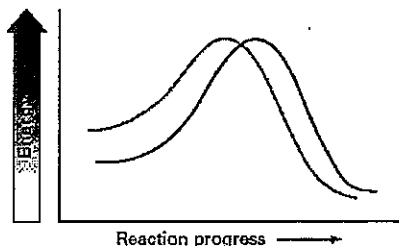
- (R)-2-bromo-2-vinylpentane
- (S)-2-bromo-2-vinylpentane
- (S)-3-bromo-3-propylbut-1-ene
- (R)-3-bromo-3-methylhex-1-ene

9. What is the relationship between these two structures?



- Identical structures
- Enantiomers
- Diastereomers
- Constitutional isomers

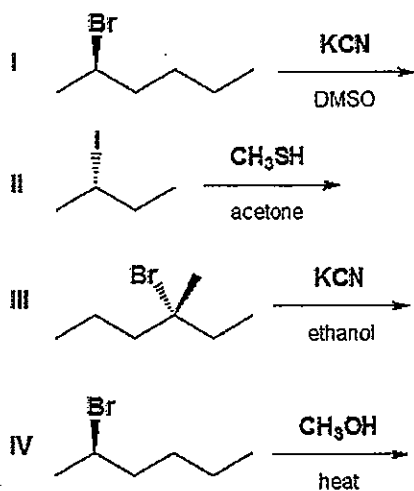
10. Consider the two lines shown on the energy diagram below.



In an  $S_N2$  reaction,

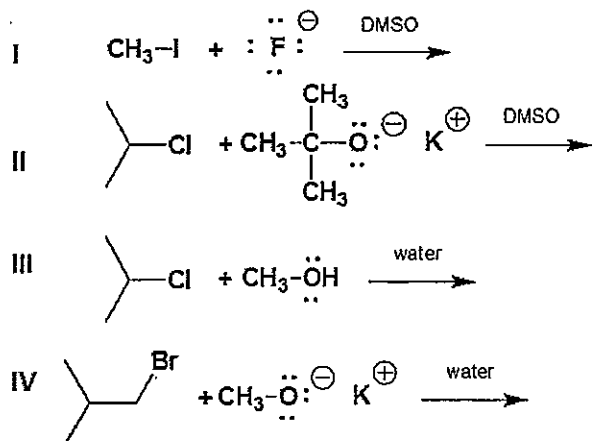
- the upper left line could represent  $H_2O$  and the lower left line  $H_2S$ .
- the upper left line could represent  $OH^-$  and the lower left line  $CH_3COO^-$ .
- the upper left line could represent  $Cl^-$  and the lower left line  $I^-$ .
- the upper left line could represent  $(CH_3)_2NH$  and the lower left line  $(CH_3)_2N^-$ .

11. Which reactions will proceed with inversion of configuration?



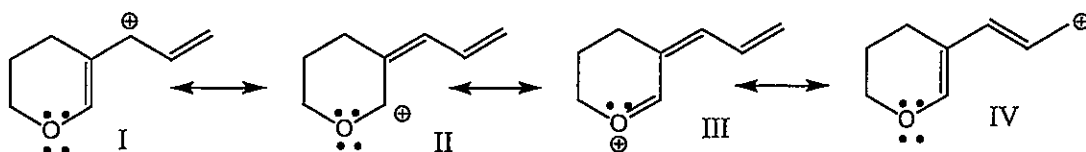
- II, III
- I, II
- III, IV
- I, IV

12. Which reaction below proceeds via an E2 mechanism?



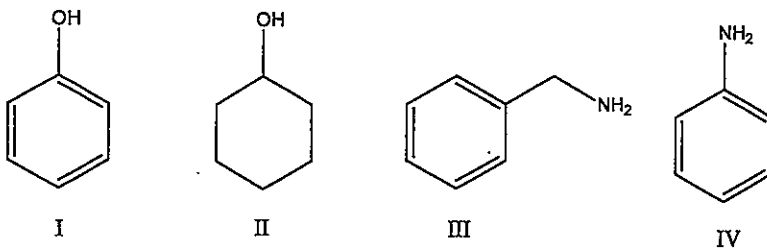
- a. I
- b. II
- c. III
- d. IV

13. Which of the following is/are the most significant resonance structure(s)?



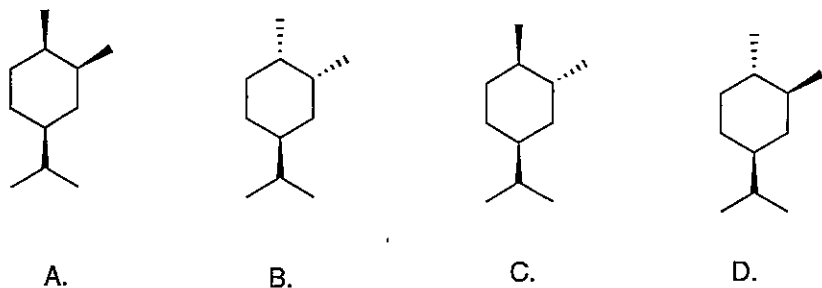
- a. I
- b. II
- c. III
- d. I & II

14. Which of the following compounds is most basic?



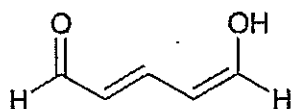
- a. I
- b. II
- c. III
- d. IV

15. Which of the following is the most stable isomer?

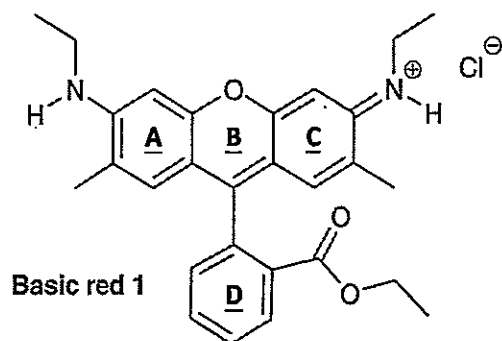


### Assay Questions (10 points each, the total is 70 points)

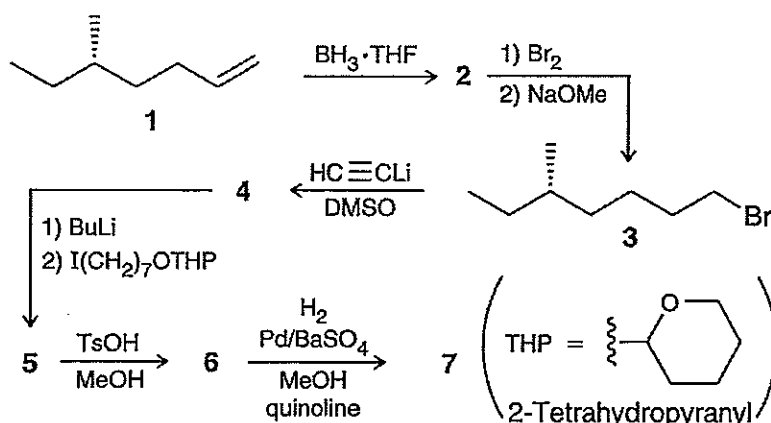
(I) In the compound below, identify all carbon atoms that are electron deficient ( $\delta^+$ ) and all carbon atoms that are electron rich ( $\delta^-$ ). Then explain your answer with resonance structures.



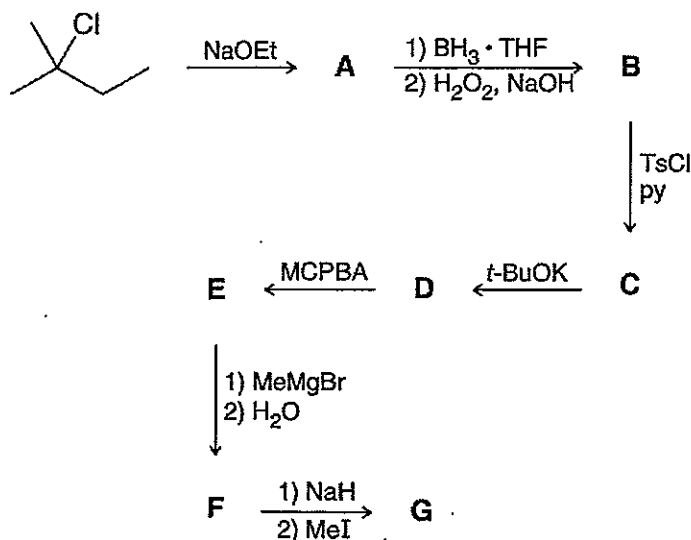
(II) Basic red 1 is a tetracyclic compound (it has four rings). This compound has many significant resonance structures, and the positive charge is highly delocalized. While resonance structures can be drawn in which the positive charge is spread throughout all four rings, nonetheless, one of the rings likely bears very little of the charge relative to the other rings. Identify the ring that is not participating as effectively in resonance and suggest an explanation.



(III) The reactions were introduced during the sex pheromone synthesis of the beetle. The conversion of compound 5 to compound 6 involves the removal of the THP group (ROTHP  $\rightarrow$  ROH), which is accomplished in acidic conditions (TsOH). Provide the structures of compounds 2, 4, 5, 6, and 7:

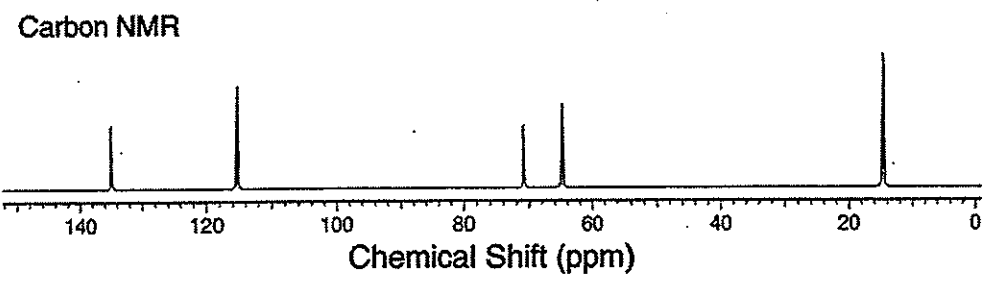
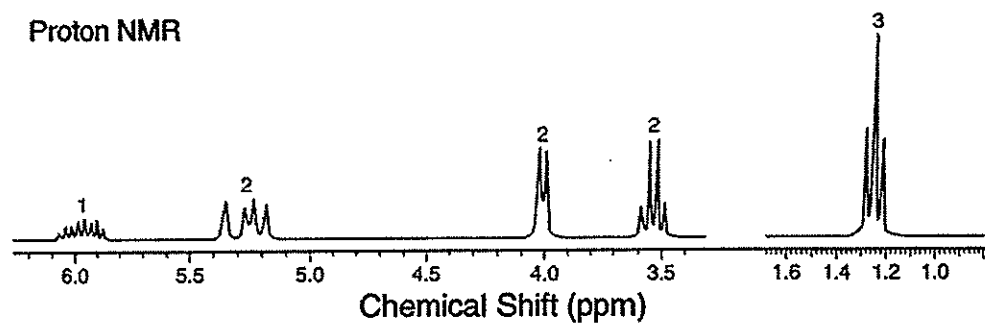
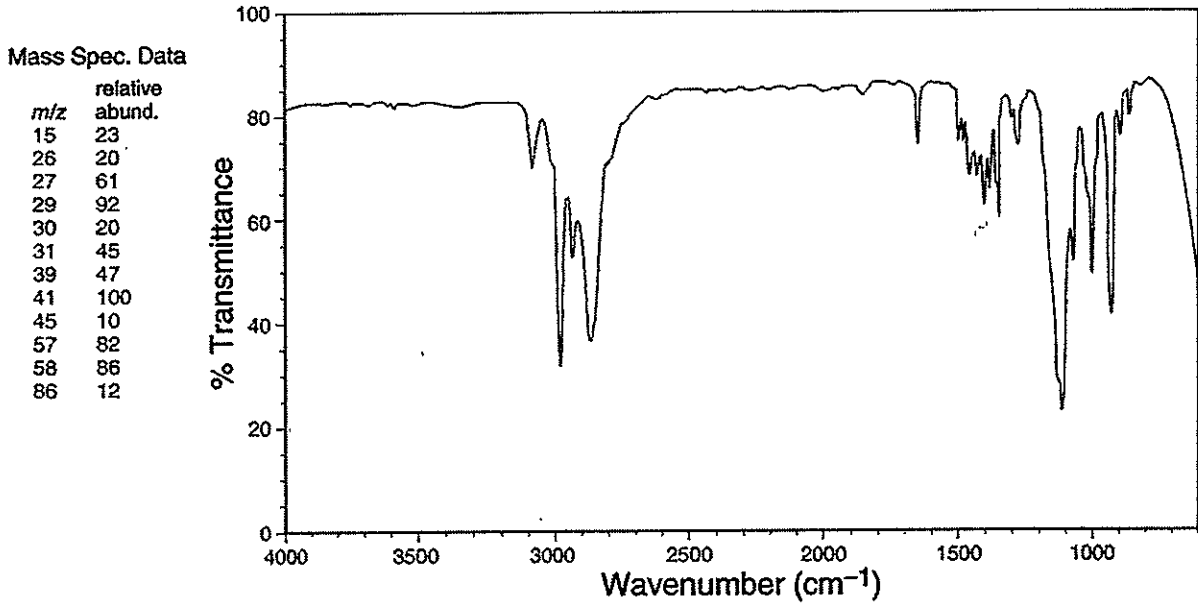


(IV) Consider the following sequence of reactions:

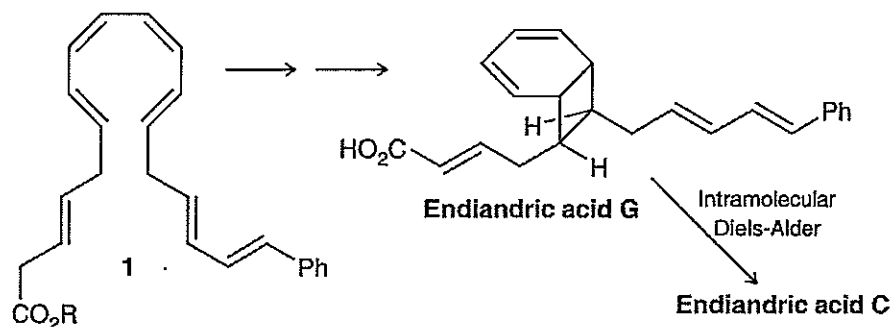


- Explain how you could use IR spectroscopy to differentiate between compounds F and G.
- If you wanted to distinguish between compounds B and F, would it be more suitable to use IR spectroscopy or mass spectrometry? Explain.
- Would mass spectrometry be helpful for distinguishing between compounds A and D? Explain.

(V) Infer the structure of a compound with molecular formula  $C_5H_{10}O$  that exhibits the following IR,  $^1H$  NMR, and  $^{13}C$  NMR spectra. Data from the mass spectrum are also provided. The answer must have the detailed thinking process.



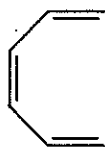
(VI) Endiandric acids, a Natural products containing chirality centers are generally found in nature as a single enantiomeric form (optically active), but the endiandric acids are an exception, as they are isolated as racemates. It has been suggested that they are formed via a series of pericyclic reactions from achiral starting materials, such as 1



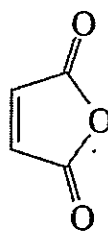
- (a) The first step in the conversion of compound 1 to endiandric acids is believed to be a thermal electrocyclic reaction to form compound 2, which possesses an eight-membered ring. Draw the structure of compound 2 and explain why it is formed as a racemic mixture.
- (b) Compound 2 can undergo another electrocyclic reaction, thereby forming the skeletal structure of endiandric acid G. Draw a mechanism for this process.

(VII)

- (a) Sketch the pi molecular orbitals of hexa-1,3,5-triene.
- (b) Show the electronic configuration of the ground state of hexa-1,3,5-triene.
- (c) Show what product would result from [6+2] cycloaddition of hexa-1,3,5-triene with maleic anhydride.



hexa-1,3,5-triene



maleic anhydride

- (d) Explain that the cyclization of hexa-1,3,5-triene with maleic anhydride is thermally forbidden but photochemically allowed.