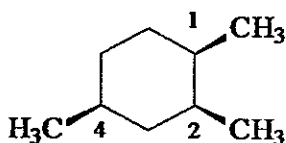


※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

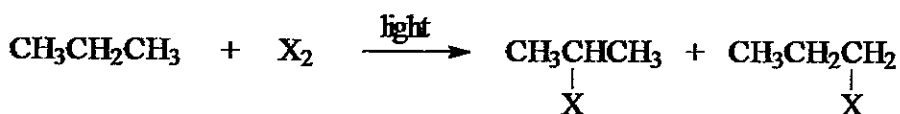
一、選擇題(單選題，40%)

1. The most stable conformation of the compound shown has:



- A. all methyl groups equatorial      B. equatorial methyl groups at C-1 and C-2, axial at C-4  
 C. equatorial methyl groups at C-1 and C-4, axial at C-2  
 D. equatorial methyl groups at C-2 and C-4, axial at C-1

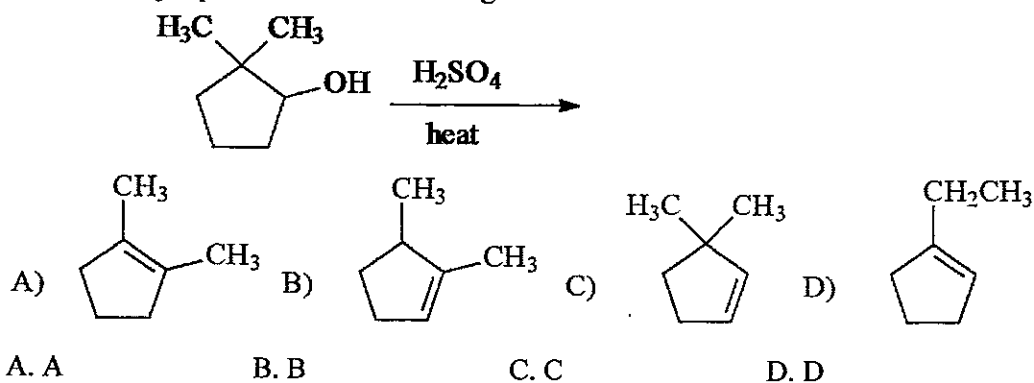
2. Consider the following reaction ( X = Cl or Br).



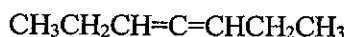
Which statement(s) is (are) correct?

- I. Statistically the 1-halopropane should be the major isomer.  
 II. The 2-halopropane to 1-halopropane ratio is largest when X=Br.  
 III. The 2-halopropane to 1-halopropane ratio is the largest when X=Cl.  
 A. only II      B. only III      C. I and II      D. I and III

3. What is the major product for the following reaction?

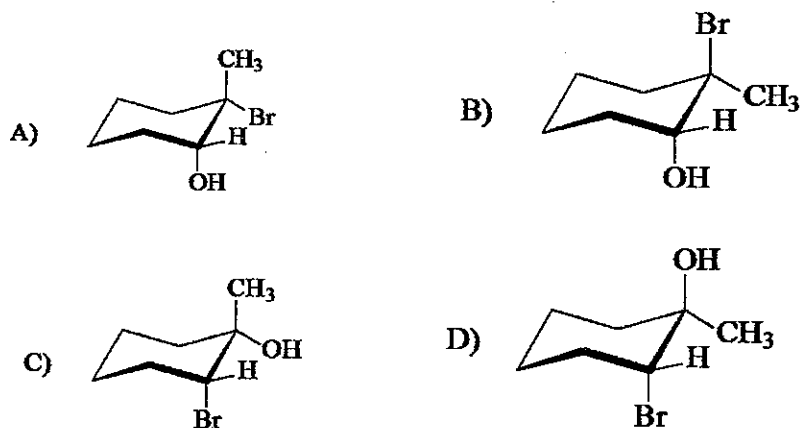


4. What type or types of stereoisomers are possible for 3,4-heptadiene, shown below?



- A. no stereoisomers are possible      B. two diastereomers, *E* and *Z*  
 C. a pair of enantiomers      D. three diastereomers, (*E,E*), (*E,Z*), and (*Z,Z*)

5. Addition of hypobromous acid, HOBr, to 1-methylcyclohexene gives:

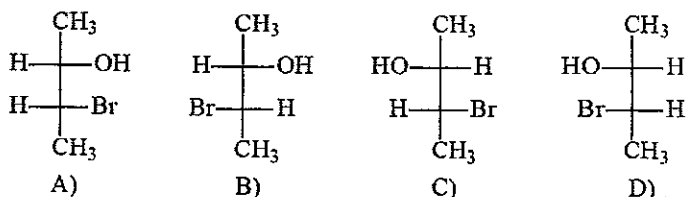
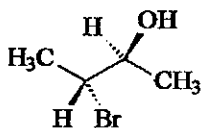


A. A                      B. B                      C. C                      D. D

6. A pure sample of (S)-phenylalanine has a specific rotation of  $+70^\circ$ . A mixture of the two enantiomers of phenylalanine has a specific rotation of  $+7.0^\circ$ . What are the percentages of the S and R enantiomers in the mixture?

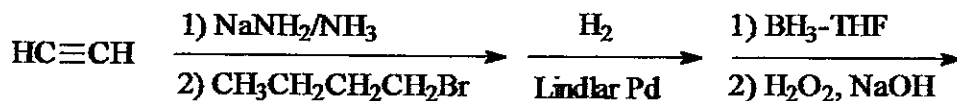
A. 95% , 5% R    B. 90% S, 10% R    C. 55% S, 45% R    D. 52.5% S, 47.5% R

7. Which of the following Fischer projections corresponds to the compound shown below?



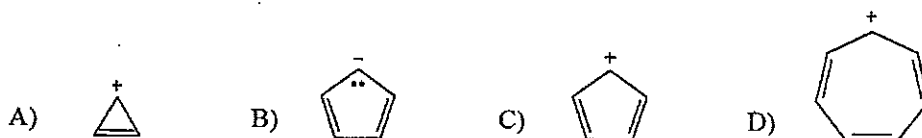
A. A                      B. B                      C. C                      D. D

8. What is the product of the following reaction sequence?



A 1-hexanol    B. 2-hexanol    C. 1,2-hexanediol    D 1-hexene

9. Which of the following ions has a ground state which is predicted to be a diradical by simple molecular orbital theory?



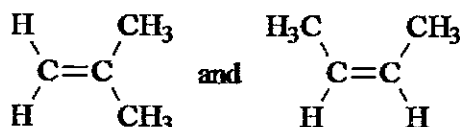
A. A                      B. B                      C. C                      D. D

10. Rank the following compounds in order of decreasing reactivity to aromatic electrophilic bromination.

I. benzene      II. toluene      III. benzoic acid      IV. phenol

A. IV > II > I > III    B. IV > III > II > I    C. II > I > IV > III    D. II > III > IV > I

11. Which of the methods below would be most useful in distinguishing between the following two compounds?

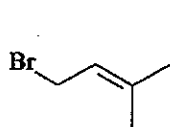
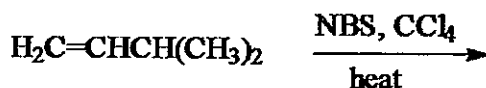


A. UV spectroscopy    B. C-13 NMR    C. IR spectroscopy    D. mass spectrometry

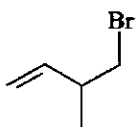
12. The reaction of *cis*-2-butene with  $\text{CH}_2\text{I}_2$  and  $\text{Zn}(\text{Cu})$  to give *cis*-1,2-dimethylcyclopropane is a(n):

A. enantiospecific reaction      B. diastereoselective reaction  
C. stereospecific reaction      D. regioselective reaction

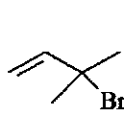
13. What is(are) the expected product(s) of the following reaction?



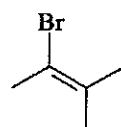
I



II



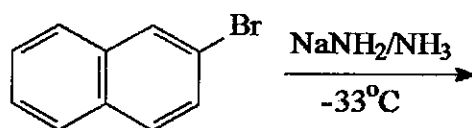
III



IV

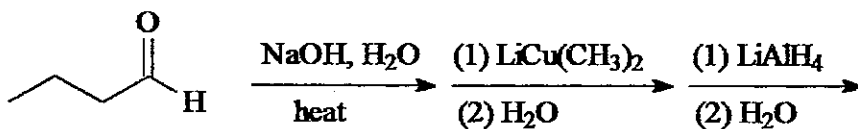
A. only II    B. only III    C. I and III    D. II and IV

14. Assume that the following reaction goes by the elimination-addition mechanism for nucleophilic aromatic substitution. Based on that, how many isomeric naphthylamines are expected in the following reaction?



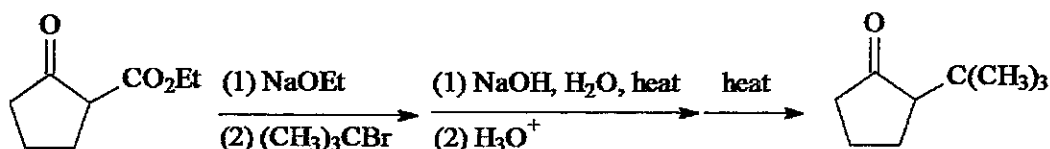
A. only a single product    B. two    C. three    D. four

15. What is the product of the following reaction sequence?



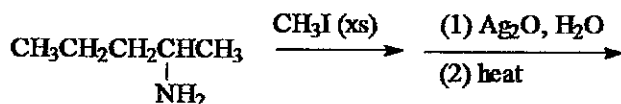
- A. 2,3-dimethyl-1-pentanol                      B. 3,3-dimethyl-1-pentanol  
 C. 3-ethyl-2-methyl-1-hexanol                D. 3-ethyl-3-methyl-1-hexanol

16. Consider the following synthetic scheme below. Which one of the following best explains why the synthesis does not work?



- A. Using NaOEt gives Claisen condensation instead of alkylation  
 B. The alkyl halide used will lead to elimination rather than alkylation.  
 C. The keto-acid formed does not decarboxylate in the last step  
 D. The base-promoted hydrolysis step does not work on the  $\beta$ -keto ester intermediate.

17. What is the major product of the reaction sequence below?



- A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$                       B)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$   
 C)  $\text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$                       D)  $\text{CH}_3\text{CH}_2\text{CH}=\underset{\text{NH}_2}{\text{C}}\text{CH}_3$

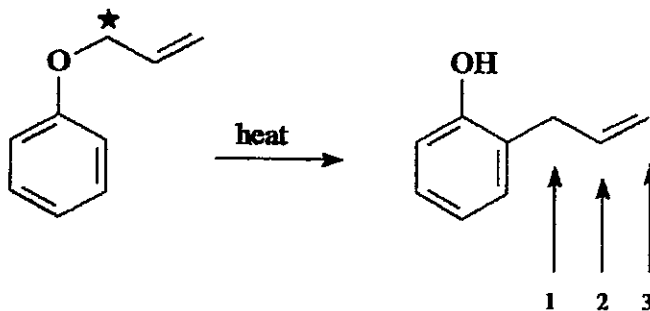
- A. A                      B. B                      C. C                      D. D

18. Rank the following compounds in order of decreasing rate of hydrolysis.

- I. acetyl chloride    II. Acetic anhydride    III. Ethyl acetate    IV. acetamide

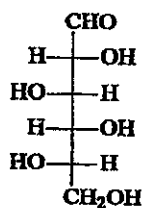
- A. I > II > III > IV    B. IV > III > II > I    C. I > III > II > IV    D. II > III > IV > I

19. Indicate where the isotopically labeled carbon atom (\*) is located in the product.

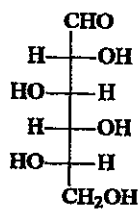


- A. #1      B. #2      C. #3      D. equally distributed between #1 and #2

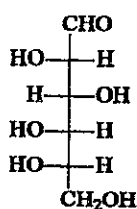
20. Which one of the following is L-(-)-glucose?



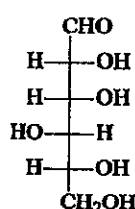
I



II



III

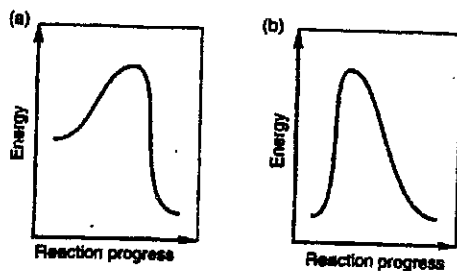


IV

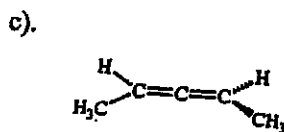
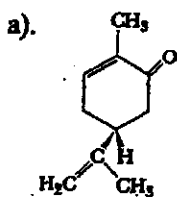
- A. I      B. II      C. III      D. IV

## 二、非選擇題 (60%)

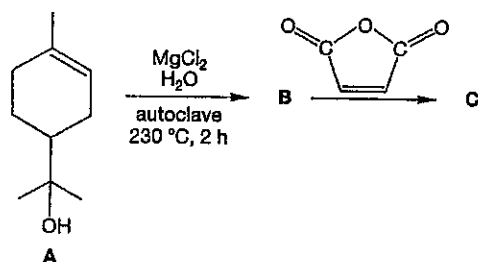
1. What is wrong with the “Energy” versus “Reaction progress” diagram shown below. (6%)



2. Give the stereo-descriptor for each of the following chiral molecules. (6%)



3. For the following reactions, please deduce the structures of compounds B and C. Spectral data for compound C are summarized below (12%)



Mass spectrum:  $m/z = 234$  (p)

IR (Nujol): 1870 (sh), 1940 (m), and 1780 (s)  $\text{cm}^{-1}$

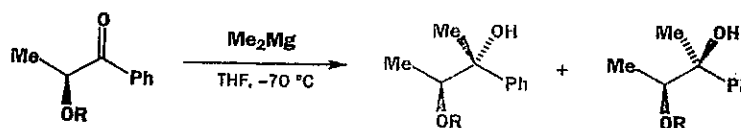
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.98 (d,  $J = 6.8$  Hz, 3H), 1.08 (d,  $J = 6.8$  Hz, 3H)

1.36 (m, 4H), 1.46 (s, 3H), 2.60 septet ( $J = 6.8$  Hz, 1H)

2.80 (d,  $J = 9$  Hz, 1H), 3.20 (d,  $J = 9$  Hz, 1H)

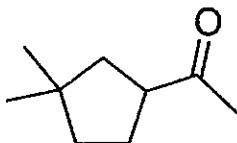
6.01 (d,  $J = 8.5$  Hz, 1H), 6.10 (d,  $J = 8.5$  Hz, 1H)

4. For the following reactions, it was found that the diastereoselectivity decreased with the protecting group changed from methyl ether to a trimethylsilyl ether and the results was summarized in the following. Please explain these observations. (10%)



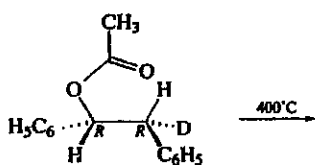
R	Ratio	Relative rate
Me	>99:1	1000
SiMe <sub>3</sub>	99:1	100
SiEt <sub>3</sub>	99:6	8
SiMe <sub>2</sub> <i>t</i> -Bu	88:2	2.5
SiPh <sub>2</sub> <i>t</i> -Bu	63:37	0.82
Si( <i>i</i> -Pr) <sub>3</sub>	42:58	0.45

5. For resolving the following racemate, a graduate student did it by reacting it with (*S*)-propane-1,2-diol to form a pair of diastereomers, then separated them with a normal silica column. After that, the student used acidic solution (HCl/H<sub>2</sub>O) to recover the pure enantiomer. However, after determining the optical rotation, it was found that it was zero, showing the method was failed.

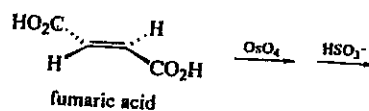


- a). what was wrong with the method? (5%)
- b). Show a correct way to resolve the racemate. (6%)
6. Give the product for the following reactions. (15%, 3% each)

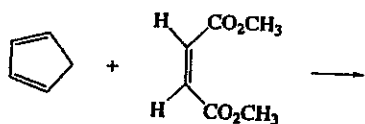
a).



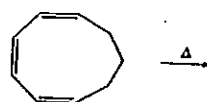
b).



c).



d).



e).

