國立成功大學

114學年度碩士班招生考試試題

編　號：42

系　所：化學系

科　目：有機化學

日　期：0211

節　次：第 2 節

注　意：1.不可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

※ 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。

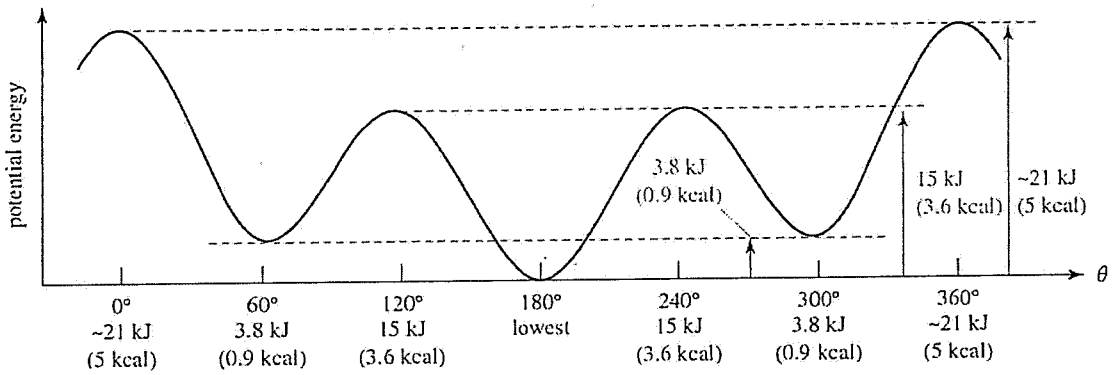
Part I. Single choice 每題兩分，總分四十分。

1. Rank the following acids in the order of increasing acidity. i) H_3O^+, ii) NH_4^+, iii) CH_3COOH, iv) CH_3CH_2OH

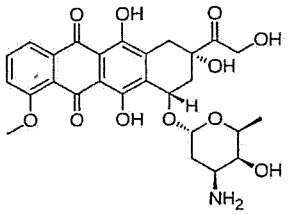
   A) iv < iii < ii < i B) iv < iii < i < ii C) ii < iv < iii < i D) iv < ii < i < iii E) iv < ii < iii < i

2. The figure below shows the potential energy changes as the *C*-*C* bond rotates. Which of the following answers matches this figure?

   A) *C*1- *C*2 of ethane B) *C*1- *C*2 of ethanal C) *C*1- *C*2 of propane D) *C*2- *C*3 of butane E) *C*1- *C*2 of propanal



3. Doxorubicin is a chemotherapy medication used to treat cancer. Which of the following statements is not true?



   A) The acetal moiety of doxorubicin is sensitive to acidic aqueous conditions.

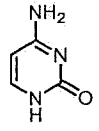
   B) The amine group-attached carbon is an asymmetric carbon, and it has the (*S*)-configuration.

   C) Doxorubicin has one secondary alcohol.

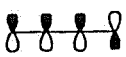
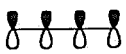
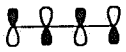
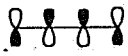
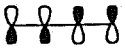
   D) Doxorubicin has one secondary amine.

   E) The olefins of doxorubicin are chemically inert due to the aromaticity.

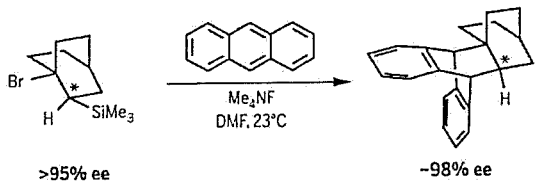
4. Based on Hückel's rule, which one is the aromatic compound?

A)  B)  C)  D)  E) 

5. The following figures represent the molecular orbitals of butadiene. Which molecular orbital is suitable to react with the LUMO of ethylene to perform a Diels-alder reaction?

A).  B).  C).  D).  E). 

6. Garg and his team reported the following reaction in Science. Nature News stated the report headline" Chemists make 'impossible' molecules that break 100-year-old bonding rule" Which of the following statements is not true?



A) The unstable reaction intermediate is known as "anti-Bredt" olefins.

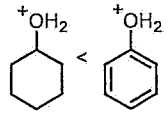
B) Bromide group of the starting material is the oxidant of this reaction.

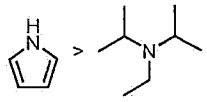
C) In this case, Diels-Alder reaction generates fused ring and bridge ring system at the same time.

D) The driving force of the first step is silicon-fluorine bond formation.

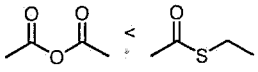
E) The key "anti-Bredt" olefin in this reaction is a bicyclo[2.2.2]octene.

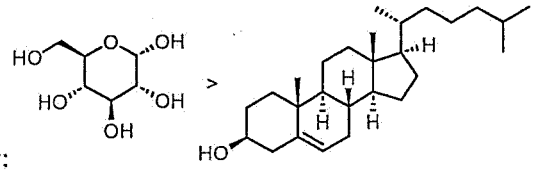
7. Which one of the following is correct?

A) Acidity: 

B) Basicity: 

C) Nucleophilicity: $F^- > HO^-$

D) Electrophilicity: 

E) Hydrophobicity: 

8. Which statements listed below is true?

A) A chiral sample gives a rotation of the plane-polarized light that is close to 180°. It is not possible to determine whether the rotation is + 180° or -180°.

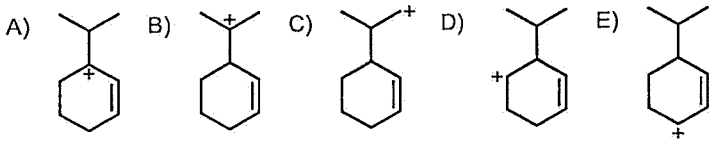
B) Asymmetric catalysis is a powerful tool to generate chiral molecules from achiral starting materials.

C) The polarimeter determines not only the (R)- or (S)- configuration of the molecule but also the direction and magnitude of rotation of the plane-polarized light.

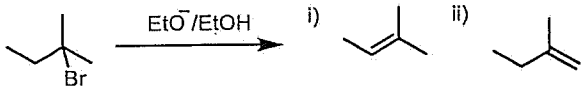
D) A mixture of enantiomer gave the specific rotation equals to zero.

E) A racemic mixture contains two achiral molecules.

9. Which of the following cation is the most unstable carbocation?

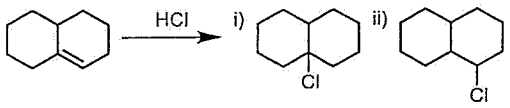


10. For the following reaction, which molecule is the major product? and is it Hoffmann or Zaitsev Product?



A) i, Hoffmann product B) ii, Hoffmann product C) i, Zaitsev product D) ii, Zaitsev product

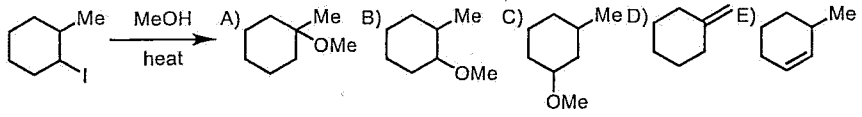
11. For the following reaction, which molecule is the major product? And does it give Markovnikov or anti-Markovnikov product?



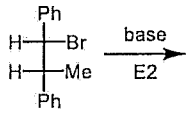
A) i, Markovnikov product B) ii, Markovnikov product C) i, anti- Markovnikov product

D) ii, anti- Markovnikov product

12. For the following reaction, which one is not the potential product?



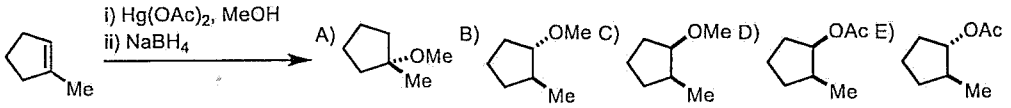
13. For the following reaction, which one is the E2 product?



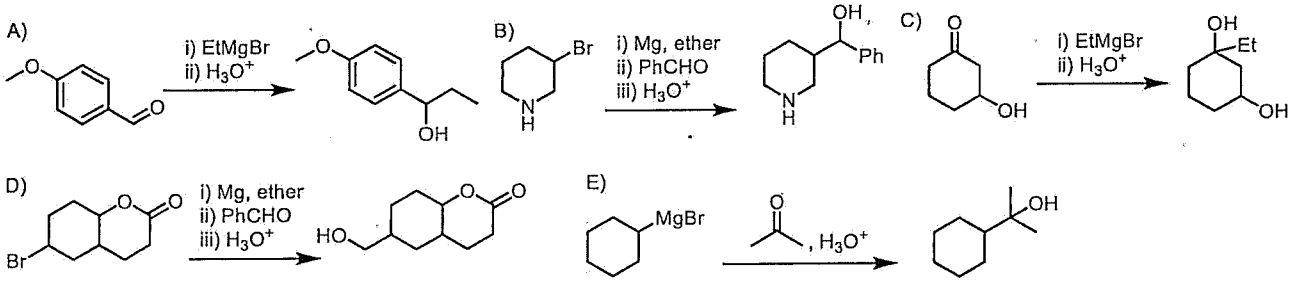
A) (*E*)-prop-1-ene-1,2-diyldibenzene B) (*Z*)-prop-1-ene-1,2-diyldibenzene C) (*E,Z*)-prop-1-ene-1,2-diyldibenzene

D) prop-2-ene-1,2-diyldibenzene E) (*E*)-prop-1-yne-1,2-diyldibenzene

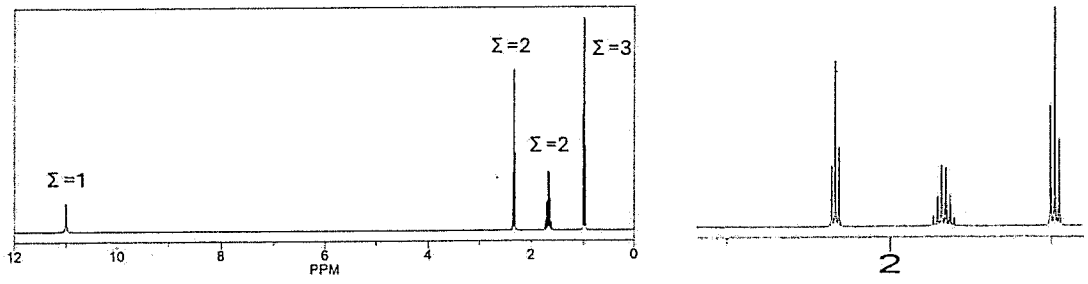
14. For the following reaction, which one is the correct product?

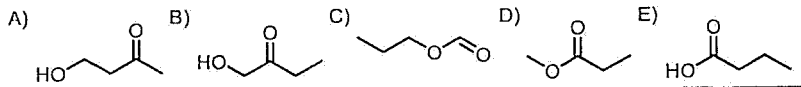


15. For the following reaction, which one can provide the desired product?

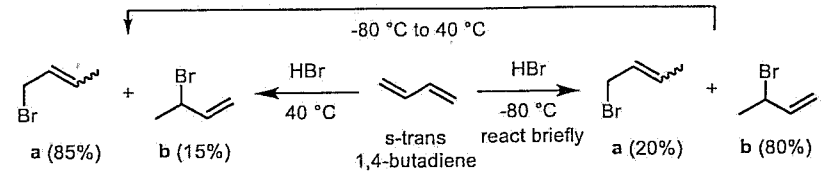


16. An unknown compound of molecular formula C_4H_8O gives the proton NMR shown here. The NMR peak at δ 11 disappears when the sample is shaken with D_2O. Which is the condensed structural formula of the unknown compound?





17. For the following reactions, which statements listed below is true?



A) In this reaction, 1,4-butadiene and bromide serve as nucleophiles.

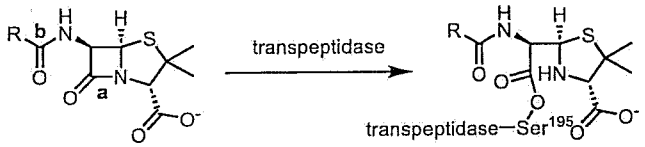
B) When treating "s-cis" 1,4-butadiene with HBr, the reaction will give **a** and **b** in different product ratios.

C) This reaction goes through radical intermediates.

D) Compound **a** has a lower activation energy, so it becomes the major product after warming up to 40 °C.

E) Compound **b** is the major product at -80 °C, so it is a thermodynamic product.

18. Antibiotic penicillin irreversibly binds to the transpeptidase enzyme and inhibits the activity through the following reaction, which statements listed below is true?



A) The driving force of this reaction is that an ester bond is more stable than an amide bond.

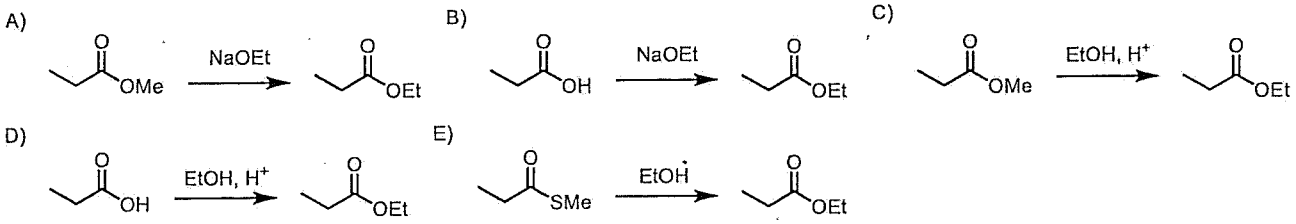
B) The entropy of this reaction is increased.

C) The enthalpy of this reaction is negative.

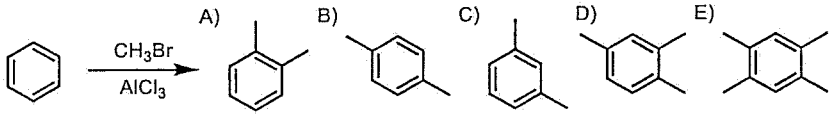
D) The Gibbs free energy of this reaction is positive at 36 °C.

E) The amide bond **b** can also be replaced to an ester bond by the same transpeptidase.

19. Which of the following reactions is not possible to obtain the desired product?



20. For the following reaction, which one is not the potential product?



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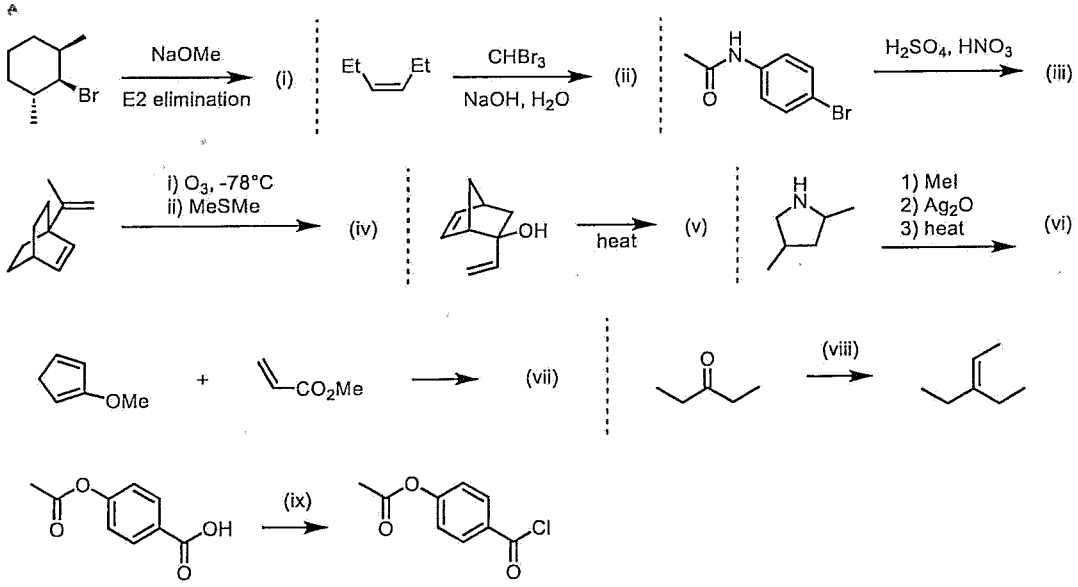
Part II. Fill in the Blank questions 每題三分，總分三十分。如所繪原子及立體結構無法判讀，不予給分。

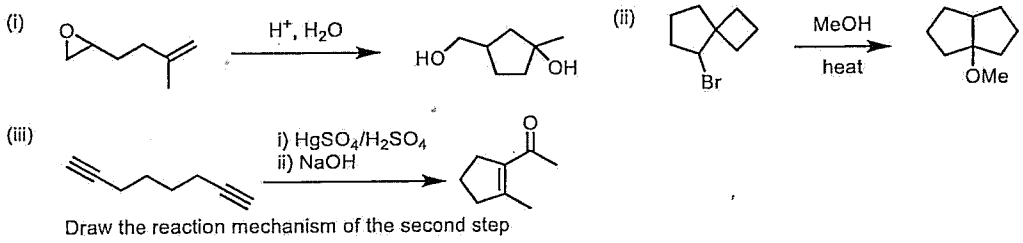
1. Please draw the most stable conformation of *cis*-1-(tert-butyl)-3-methylcyclohexane.

2. Please provide proper reagents or molecules with proper stereochemistry for the following incomplete reactions.



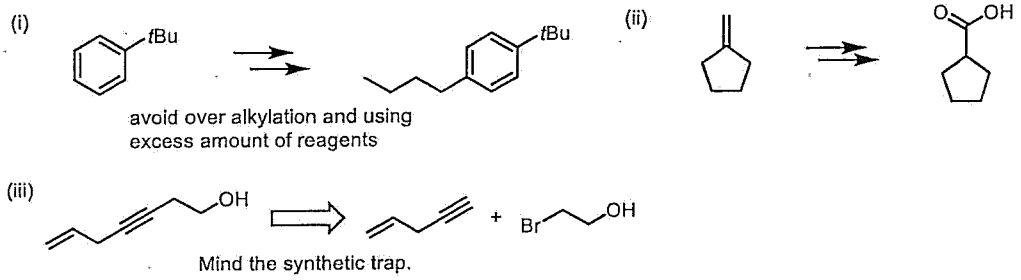
Part III. Please answer the following questions. 每題五分，總分三十分。

1. Propose mechanisms for the following reactions



Draw the reaction mechanism of the second step

2. Please propose reasonable synthetic routes for the following transformations. (less than 5-step)



avoid over alkylation and using excess amount of reagents

Mind the synthetic trap.