國立成功大學

115學年度碩士班招生考試試題

編　號：36

系　所：化學系

科　目：有機化學

日　期：0203

節　次：第 2 節

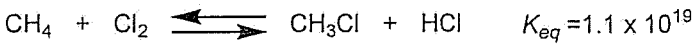
注　意：1.不可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

Part I. Single choice 每題兩分，總分十八分。

1. In a polar protic solvent (e.g., water or methanol), rank the following species in order of increasing nucleophilicity (lowest → highest): (i) $MeNH_2$, (ii) MeO^-, (iii) iPr_2EtN, (iv) MeS^-.

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

2. Chlorination of methane is an important industrial reaction that is initiated by light or heat. Which of the following statements is NOT true?



   A) Although the chlorination reaction is exothermic and can lead to the formation of polychlorinated products, the reaction can be controlled to favor monochlorinated methane by adjusting the ratio of the reactants.

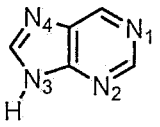
   B) A value of $K_{eq} > 1$ for this reaction indicates that the Gibbs free energy change is positive and that the reaction is thermodynamically spontaneous.

   C) The observation of ethane formation indicates that the reaction proceeds via a radical mechanism.

   D) This reaction is an oxidation–reduction reaction.

   E) The reaction is dominated by enthalpy changes rather than entropy changes.

3. Purine consists of an imidazole ring fused to a pyrimidine ring. It contains three basic nitrogen atoms and one non-basic (non-proton-accepting) nitrogen. Which nitrogen atom is non-basic?



   A) N_1 B) N_2 C) N_3 D) N_4

4. The following figures represent the molecular orbitals of ethylene. Which of the following statements is NOT true?

   A) In the photochemical [2+2] cycloaddition of ethylene, one electron is promoted from the HOMO, allowing interaction between two excited ethylene to form the product.

   B) Ethylene has the largest HOMO–LUMO energy gap among simple conjugated polyenes, such as buta-1,3-diene and 1,3,5-hexatriene.

   C) In the [4+2] cycloaddition between ethylene and buta-1,3-diene, the diene is electron-rich and reacts through its HOMO with the LUMO of ethylene.

   D) The [4+2] cycloaddition between ethylene and buta-1,3-diene is a concerted reaction that proceeds through a symmetry-allowed transition state.

   E) Orbital i corresponds to the HOMO of ethylene, and orbital ii corresponds to the LUMO of ethylene.

5. Please rank the acidity of following protons (lowest → highest):

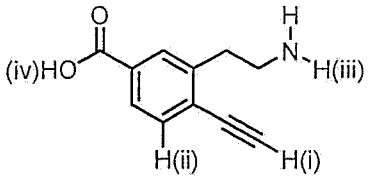
A) (ii) benzene < (iii) primary amine < (i) terminal alkyne < (iv) carboxylic acid

B) (iii) primary amine < (ii) benzene < (i) terminal alkyne < (iv) carboxylic acid

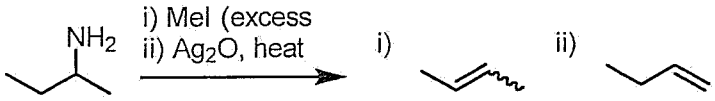
C) (ii) benzene < (i) terminal alkyne < (iii) primary amine < (iv) carboxylic acid

D) (iii) primary amine < (i) terminal alkyne < (ii) benzene < (iv) carboxylic acid

E) (i) terminal alkyne < (ii) benzene < (iii) primary amine < (iv) carboxylic acid

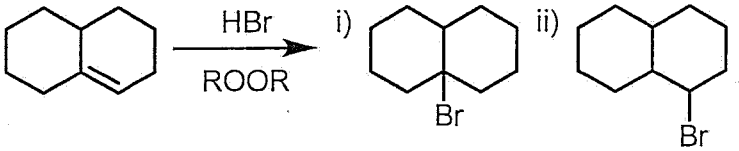


6. For the following reaction, which molecule is the major product? and is it Hoffmann or Zaitsev Product?



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

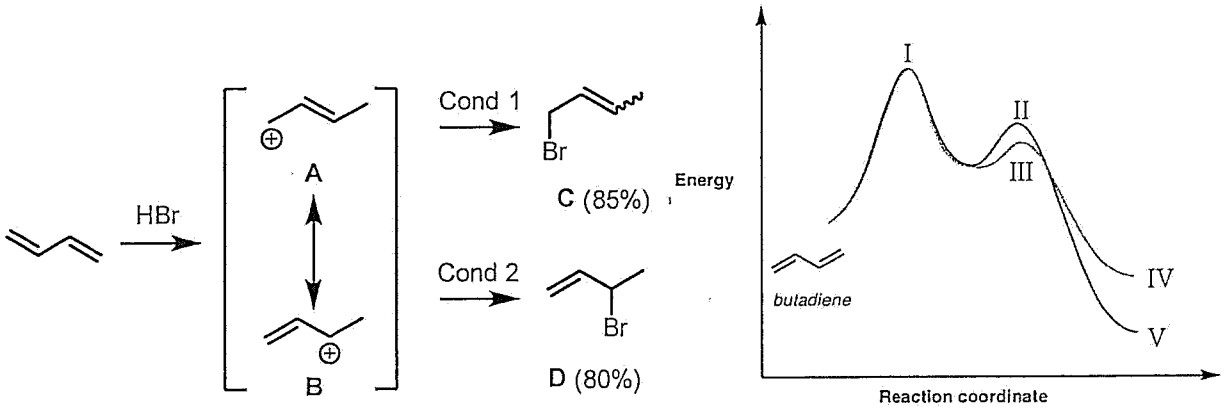
7. For the following reaction, which molecule is the major product? And does it give Markovnikov or anti-Markovnikov product?



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

D) ii, anti- Markovnikov product

8. For the following reactions, which statement listed below is NOT true?



A) Compound **C** and **D** are constitutional isomers, and compound **C** contains diastereomers.

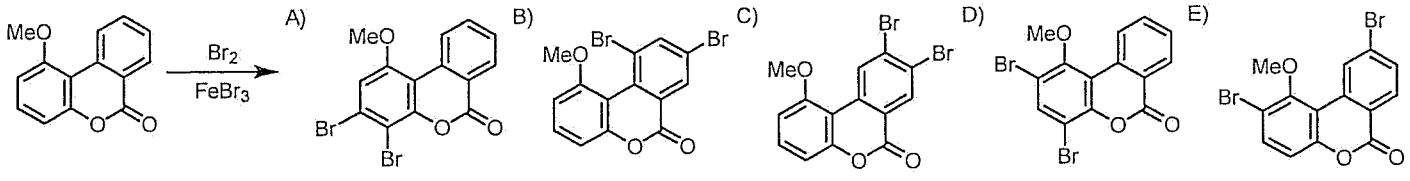
B) A primary cation has higher energy than a secondary cation.

C) A transition state (TS) has partially formed and partially broken bonds and cannot be isolated.

D) Cation **A** with the highly substituted double bond represents TS **III**, and cation **B** represents TS **II**.

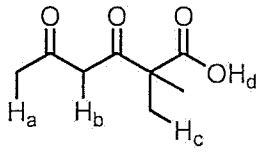
E) At lower temperatures, compound **D** with the less substituted double bond is the major product **IV**.

9. For the dibromination of the following aromatic compound, which is the major product?

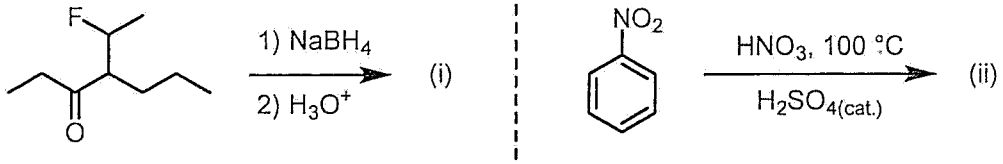


Part II. Fill in the Blank questions 每子題三分，總分三十分。

1. Rank all the distinct types of hydrogen atoms in the following molecule in order of decreasing acidity. (3 points)

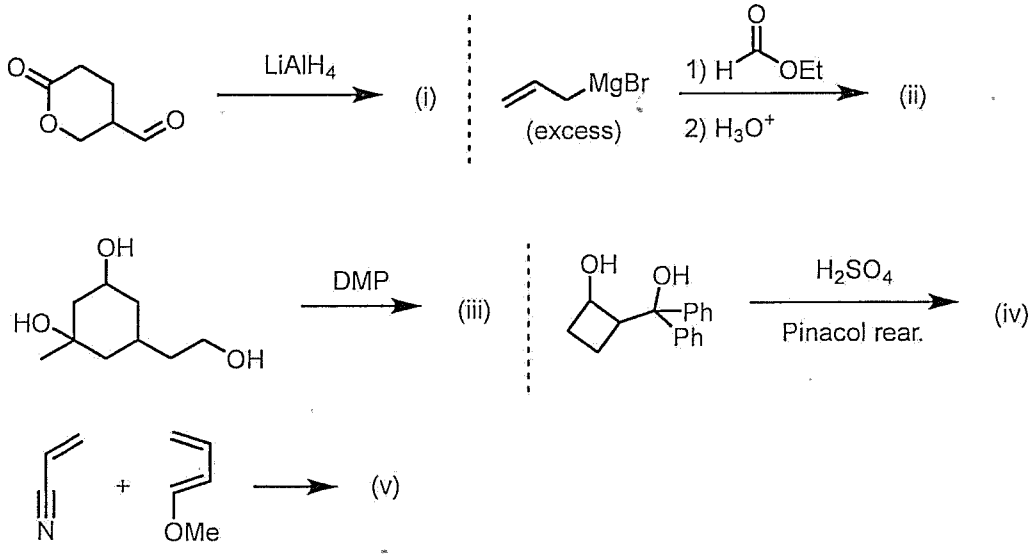


2. Please provide the chemical structures (2 points) and IUPAC names (1 points) of the products of the following reactions. (6 points in total)



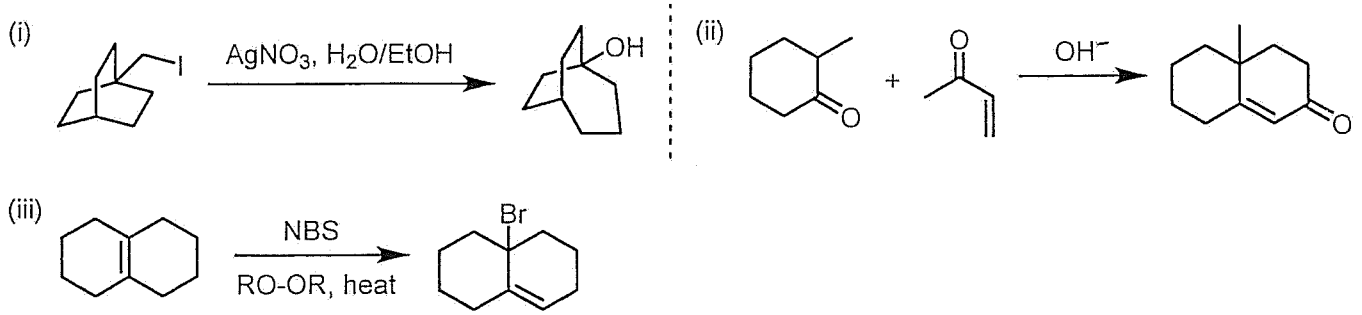
3. The specific rotation of enantiomerically pure (+)-butan-2-ol is +13.5°, as measured using a polarimeter equipped with a 100-mm polarimeter tube and a sample concentration of 1.0 g mL^{-1}. (6 points in total)
(i) Calculate the **specific rotation** of a mixture containing 3.0 g of (+)-butan-2-ol and 7.0 g of (-)-butan-2-ol, assuming the total volume of the mixture is unchanged. (mind the units and the positive/negative sign.)
(ii) Using the same polarimeter and tube length, an enantiomerically pure sample of (-)-butan-2-ol gives an observed rotation of -3.5°. What is the **concentration** of this sample in g mL^{-1}?

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

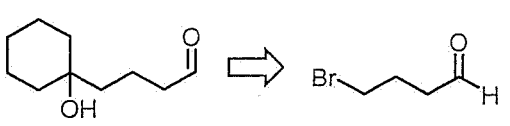


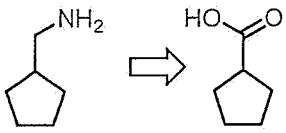
Part III. Please answer the following questions. 每子題五分，總分三十分。

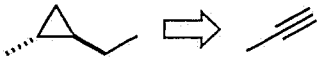
1. Propose mechanisms for the following reactions



2. Please propose reasonable synthetic routes.

(i) 

(ii) 

(iii) 

Part IV. Please answer the following questions. 總分二十二分。

1. (*E*)-but-2-ene is a liner alkene with four carbon atoms.
   (i) Under which of the following reaction conditions, (*Z*)-but-2-ene will give a meso-compound? (3 points)
   A) $OsO_4 + H_2O_2$ B) $CH_3CO_3H + H_3O^+$ C) $Pd/C + H_2$ D) $Cl_2 + H_2O$ E) Br_2.
   (ii) When (*E*)-but-2-ene is subjected to catalytic hydrogenation ($Pd/C + H_2$), a single product is obtained. Draw the Newman projection along the C2–C3 bond of the most stable conformation of the product. (3 points)

2. *cis*-But-2-ene reacts with Br_2 to give a vicinal dibromide.
   (i) Draw the product in a Fischer projection. (3 points)
   (ii) Indicate the configuration (chirality) of the asymmetric carbon atoms. (3 points)
   (iii) Are the brominated products optically active? Explain your answer. (3 points)

3. When 1-bromo-4-(tert-butyl)cyclohexane undergoes an E2 elimination:
   (i) Which is more favorable, (A) the *cis*-1-bromo-4-(tert-butyl)cyclohexane or (B) the *trans*-1-bromo-4-(tert-butyl)cyclohexane isomer? Explain your answer. (3 points)
   (ii) Draw the most stable chair conformation of *cis*-1-bromo-4-(tert-butyl)cyclohexane. (4 points)