國立成功大學八十四學年度化学研究構試(有机化学

2.

Explain the following terms and give an example.
(a) mesomeric effect (resonance effect)

(6%)

- (b) meso compound
- (c) pericyclic reaction

Predict the major product for each of the following reactions.

(10%)

(a)
$$\longrightarrow$$
 CHO + H₃C- $\stackrel{\circ}{\text{C}}$ \longrightarrow $\stackrel{\text{H}^+}{\longrightarrow}$

(b)
$$H_3$$
 H_3 C H_3 C

(c)
$$H_2C=CH-C-CH_2OH$$
 1) DMSO, (COCI)₂ 2) NH_2OH

3. Starting with any organic compound of less than four carbon atoms and any inorganic material. Synthesize the compound

$$(\Pi)$$

- 4. Starting with ethylene oxide and methyl iodide as the only organic materials and any inorganic compound. Synthesize alanine, CH₃CH(NH₂)COOH, an important amino acid. (5%)
- 5. Propose an efficient synthesis of glyceraldehyde from acrolein. (4/2)

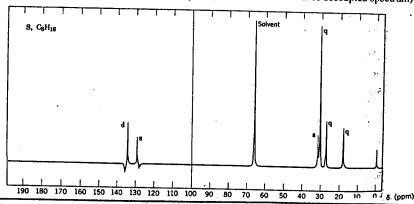
 OH

 CHO

 HOCH₂-C-CHO

6. The well known indicator, phenolphthalein, undergoes the following changes as a neutral solution is made successively basic. Some of these forms are colorless, some intensely colored. Which would you expect to absorbe at sufficient long wavelength to be visible? Give your reasoning. (5%)

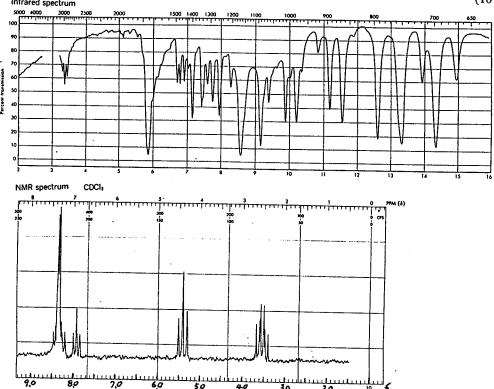
7. Compound S can decolorize a solution of bromine in carbon tetrachloride. The elemental analysis for this compound gave: C, 85.71%; H, 14.28%. The mass spectrum showed the molecular ion peak at m/z = 112. The proton-decoupled ¹³C NMR spectrum is given below. Propose a structure for this compound S. (The letters s, d, and q refer to signal splitting (singlet, doublet and quartet) in the ¹H off-resonance decoupled spectrum)



國立成功大學八十四學年度化学研究研試(历初代学 試題)第2頁

8. Ozonolysis of 1-phenyl-1-cyclopropyl-2-propyn-1-ol gave a 15% yield of minor product with molecular formula $C_{11}H_{10}O_2$. Hydrogenation (platimum oxide, methanol) resulted in the absorption of slightly more than one equivalent of hydrogen. The IR and ¹H NMR spectra are shown below. Propose a structure for this product.

Infrared spectrum (10%)



第二部份

- 1. The chlorination at C2 of (S)-2-bromobutane gives a 1:1 mixture of enantiomers. Does the reaction at C3 also give an equimolar mixture of diastereomers? Please account for your answer. (5%)
- 2. For the racemic mixture of 1-phenylethylamine, please show a method to resolve this mixture. (4%)
- 3. Muscarine is a poisonous substance present in mushroom *Amanita muscaria*. Its structure is represented by the constitution shown below.

- (a). Including muscarine, how many stereoisomers have this constitution? (3%)
- (b). Muscarine has the configuration 2S,3R,5S. Write a structural formula of muscarine showing its correct stereochemistry. (2%)
- 4. No reaction is observed when the process is carried out under the condition shown as the following. However, when crown ether, 18-crown-6, is added, the reaction preceeds to give 92% of 1-fluorooctane. Please explain this fact. (4%)

CH₃(CH₂)₆CH₂Br KF, benzene, 90°C

國立成功大學八十四學年度此学研究的考試(有私化学 試題)等 3頁

- 5. (a). Can you suggest a possible explanation for the fact that the 1,2-addition reaction of 1,3-butadiene and hydrobromide occurs faster than 1,4-addition? (3%)
 - (b). How can you account for the fact that the 1,4-addition product is more stable? (3%)
 - (c). The 1,4-addition is said to be under thermodynamic control while 1,2-addition under kinectic control. Please plot a potential energy versus reaction coordinate diagram to illustrate the reaction pathway of 1,2-and 1,4-additions. (3%)
- 6. Even though the methyl group occupies an equatorial position, the following conformation is not the most stable one for methylcyclohexane. Explain why, and draw the most stable conformation of this compound. (4%)

- 7. For this statement " when an achiral intermediate is formed from an optically active precursor, optically inactive products result ", please give an example to illustrate this statement. (4%)
- 8. The reaction of cyclopentyl bromide with sodium cyanide to give cyclopentyl cyanide proceeds faster if a small amount of NaI is added to the reaction mixture. Can you suggest a reasonable mechanism to explain the catalytic function of NaI? (3%)

$$\begin{array}{|c|c|c|c|c|c|}\hline & H & \frac{NaCN}{ethanol-water} & \hline & H \\ \hline & CN & \\ \hline \end{array}$$

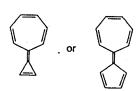
9. Alkynes are more acidic than alkenes and alkenes are more acidic than alkanes. i.e.

HC=CH > CH₂=CH₂ > CH₃CH₃
Acetylene Ethylene Ethane

$$K_a = 10^{-26}$$
 $\sim 10^{-45}$ $\sim 10^{-62}$

Please explain why. (3%)

10. Which one of the followings should be stabilized by resonance to a greater extent? Please account for your answer. (3%)



- 11. (a). Please set up a method (experiment) to evaluate the relative stabilities of the four isomeric alkenes of C₄H₈.
 - (b). It is known that the stability trend is: 2-methylpropene > trans-2-butene > cis-2-butene > 1-butene. Please show the principal factors that make one alkene more stable than another. (3%)