

國立中山大學100學年度碩士班招生考試試題

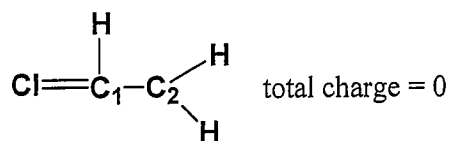
科目：有機化學及無機化學【化學系碩士班】

有機化學 (50 points)

(一) Multiple choice questions, choose only one answer. (3% x 10 = 30%)

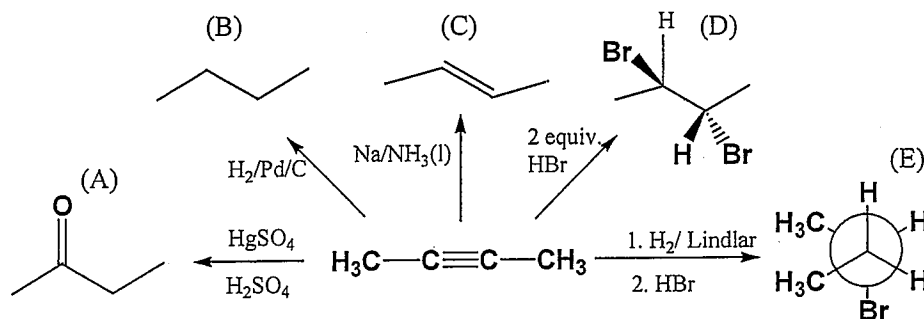
1. Which of the following is NOT a reactions between Lewis acid-base

- (A) $(\text{CH}_3)_3\text{N} + \text{BF}_3 \rightarrow (\text{CH}_3)_3\text{NBF}_3$ (B) $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$
 (C) $\text{PF}_3 + \text{F}_2 \rightarrow \text{PF}_5$ (D) $\text{SnCl}_2 + \text{Cl}^- \rightarrow \text{SnCl}_3^-$ (E) $\text{Al}(\text{OH})_3 + \text{HO}^- \rightarrow \text{Al}(\text{OH})_4^-$

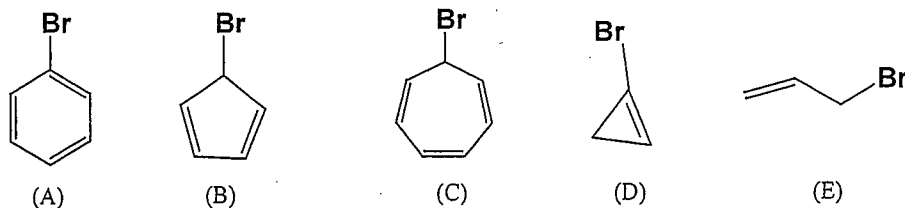
2. The formal charge on C_1 and C_2 for the molecule below are:

- (A) $\text{C}_1 = \text{C}_2 = 0$ (B) $\text{C}_1 = -1, \text{C}_2 = +1$ (C) $\text{C}_1 = 0, \text{C}_2 = +1$
 (D) $\text{C}_1 = +1, \text{C}_2 = 0$ (E) $\text{C}_1 = 0, \text{C}_2 = -1$

3. Which of these reactions below will not give the product shown.



4. Which of the following bromides would ionize most rapidly to form a carbocation?



5. Which of the following compound(s) below can be oxidized by PCC (pyridinium chlorochromate) in dry dichloromethane as solvent to give carbonyl product.

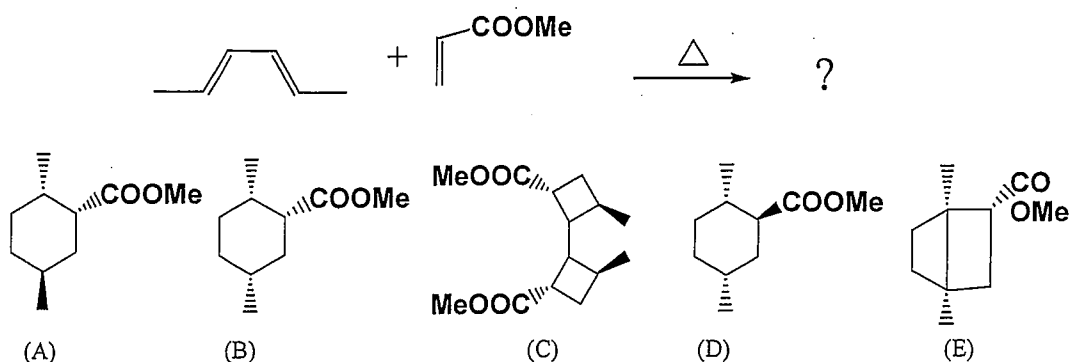
- (I) 1-methylcyclopentanol (II) 4-hydroxy-4-methyl-2-pentanone
 (III) cyclohexanecarbaldehyde (IV) cyclohexyl ethyl ether

- (A) (I) (B) (I) and (II) (C) (I), (II) and (III) (D) (II) (E) (IV)

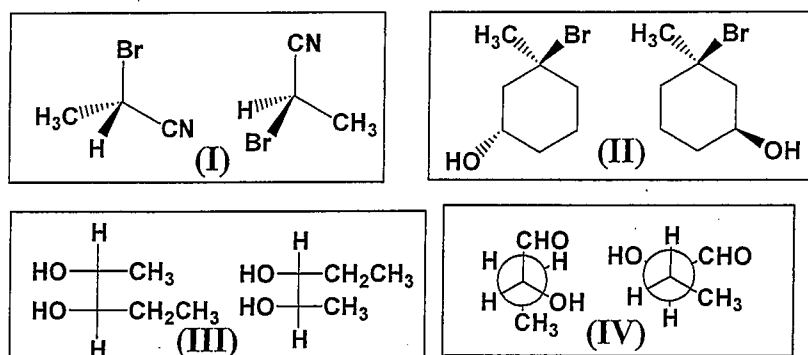
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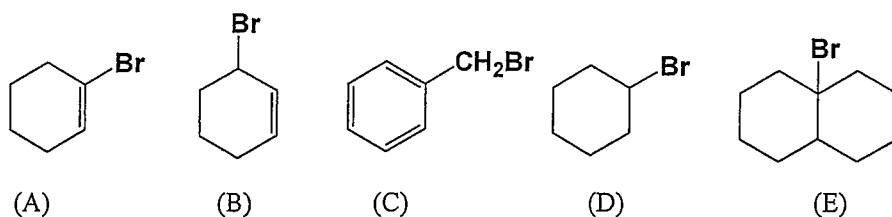
6. Choose the correct product for the Diels-Alder reaction below:



7. Which set of compounds below is enantiomeric?



(A) (I) (B) (I), (II) (C) (I), (III) (D) (I), (IV) (E) (IV)

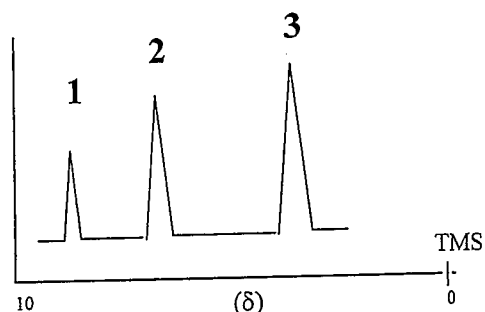
8. Which of the following **cannot** undergo nucleophilic substitution9. Which statement is **correct** for S_N1 reaction at the chiral carbon atom?

- (A) The product will be optically active, but with Walden inversion
- (B) A carbanion is formed as an intermediate
- (C) The product will be a racemic mixture
- (D) The rate of reaction is a function of the concentration of the nucleophile
- (E) The attacking group will be a strong electrophile

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10. Base on the low-resolution proton NMR spectrum of a particular compound shown below, which of the following is (are) true?

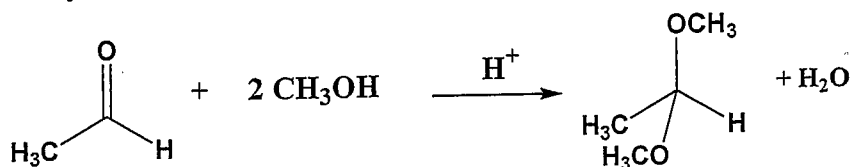


- I. There are at least three different types of protons in this compound
- II. Protons at peak 2 are more shielded than those in peak 1
- III. Proton in peak 3 is most deshielded in this compound
- IV. Proton in peak 1 is most shielded in this compound

- (A) I (B) (I) and (II) (C) (I) and (III) (D) (I) and (IV) (E) (III)

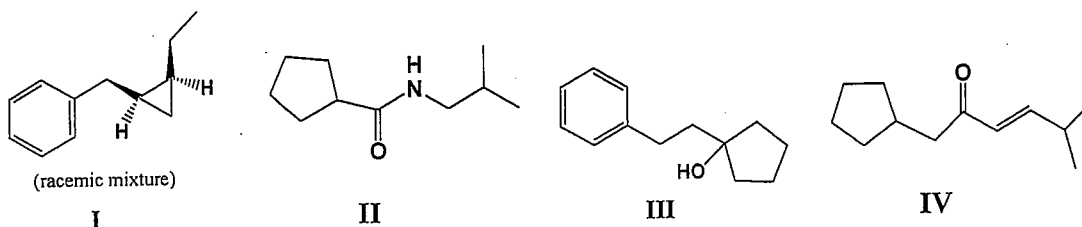
(二). Mechanism question (5% x 1 = 5%)

Propose mechanisms for the following reaction. Be sure that your diagrams clearly show what you want your answer to mean.

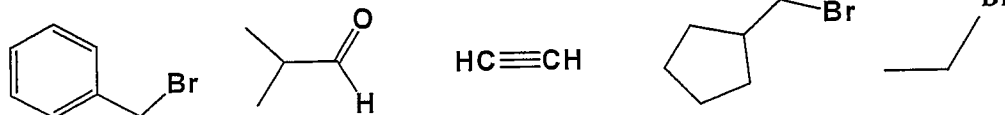


(三). Synthetic question (5% x 3 = 15%)

Choose **THREE** compounds below, **I**, **II**, **III** and **IV**; and design the synthesis of each of the compound from the given starting materials (carbon containing). Give a detail step by step synthesis, showing all the product form in each step. Also, indicate clearly all the other common reagents needed for the transformation in each step.



Starting Materials You may choose from to synthesis I, II, III, IV



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無機化學 (50 points)

(四) Answer the following questions: (30 points; 3 points for each question)

1. Give the IUPAC name of $K_3[Fe(CN)_6]$.
2. Determine the metal-metal bond order consistent with the 18-electron rule for the compound of $[(\eta^5-C_5H_5)Mo(CO)_2]_2^{2-}$.
3. Determine the point group for stagger ferrocene $((\eta^5-C_5H_5)_2Fe)$.
4. **Explain briefly** the trend of π bonding characteristics (B-X bond distances in BF_3 (131 pm), BCl_3 (174 pm), BBr_3 (189 pm), and BI_3 (210 pm)).
5. Consider the molecule $CH_3C \equiv CH$. Apply Bent's rule to predict whether the bond angles, H-C-H, are greater or less than 109.5° . **Please give brief explanation.**
6. Of the compounds $[Cr(CN)_5(NO)]^{4-}$, $[Mn(CN)_5(NO)]^{3-}$, and $[Fe(CN)_5(NO)]^{2-}$, which would you expect to have the highest energy $\nu(NO)$ stretching band in the IR spectrum. **Please give brief explanation.**
7. Determine the metal-metal bond order for $[Re_2Cl_4(PMe_2Ph)_4]^+$.
8. **Briefly explain** the band theory.
9. Which ion, Mg^{2+} or Ba^{2+} , will exhibit the greater polarizing power? **Please give brief explanation.**
10. **Briefly explain** the trans-effect.

(五) Give the most stable molecular structure of $P(CH_3)_2F_3$? What would the variable temperature ^{19}F -NMR spectra of $P(CH_3)_2F_3$ look like under the condition of very slow fluorine exchange. Only consider the spin-spin interactions of F-F and F-P. **Give your explanation.** (10 points)

(六) Answer the following questions for the octahedral high-spin complex of $[FeL_6]^{2+}$ (L = neutral mono-dentate ligand):

1. Determine the ground-state term symbol for the free iron (Fe) ion. **Give your explanation.** (2 points)
2. What is the electronic ground-state irreducible representation for this complex? **Give your explanation.** (4 points)
3. Would you expect the contribution of Jahn-Teller effect for this complex? **Give your explanation.** (4 points)