

國立中山大學 108 學年度 碩士暨碩士專班招生考試試題

科目名稱：物理化學及分析化學【化學系碩士班】

—作答注意事項—

考試時間：100 分鐘

- 考試開始響前不得翻閱試題，並不得書寫、劃記、作答。請先檢查答案卷（卡）之應考證號碼、桌角號碼、應試科目是否正確，如有不同立即請監試人員處理。
- 答案卷限用藍、黑色筆(含鉛筆)書寫、繪圖或標示，可攜帶橡皮擦、無色透明無文字墊板、尺規、修正液（帶）、手錶(未附計算器者)。每人每節限使用一份答案卷，不得另攜帶紙張，請衡酌作答。
- 答案卡請以 2B 鉛筆劃記，不可使用修正液（帶）塗改，未使用 2B 鉛筆、劃記太輕或污損致光學閱讀機無法辨識答案者，其後果由考生自行負擔。
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- 可否使用計算機請依試題資訊內標註為準，如「可以」使用，廠牌、功能不拘，唯不得攜帶具有通訊、記憶或收發等功能或其他有礙試場安寧、考試公平之各類器材、物品（如鬧鈴、行動電話、電子字典等）入場。
- 試題及答案卷（卡）請務必繳回，未繳回者該科成績以零分計算。
- 試題採雙面列印，考生應注意試題頁數確實作答。
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題號：422002

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分析化學(50%)

選擇題(單選題，每題兩分，共十五題)

01. To determine whether the variances of two analytical methods are significantly different from each other, which of the following tests should be conducted?
- Student's t test
 - F test
 - Q test
 - Y test
02. Which of the following statements is INCORRECT?
- $2 \text{ ppb Hg}^{2+} = 10 \text{ nM Hg}^{2+}$ (Atomic mass of Hg is 200 amu).
 - The number 0.01808 has five significant figures.
 - $0.2 (\pm 0.01) + 0.1 (\pm 0.02) - 0.1 (\pm 0.02) = 0.2 (\pm 0.03)$.
 - 5% (w/v) aqueous silver nitrate corresponds to a solution prepared by dissolving 0.5 g of silver nitrate in sufficient water to give 10 mL of solution.
03. Which of the following statements concerning the operation of laboratory glassware in analytical experiments is INCORRECT?
- A desiccator is used to store dried materials.
 - Filtering crucibles serve as containers and filters.
 - Burets are commonly used in the titration-related experiments
 - Volumetric flasks are usually calibrated to deliver.
04. Which of the following statements concerning systematic errors and random errors is INCORRECT?
- Random errors can be detected and corrected by calibration.
 - Analysis of standard reference materials can be used to estimate the bias of an analytical method
 - Over repeated measurements, the obtained random error follows a Gaussian distribution.
 - Absorption of CO_2 by a standardized solution of NaOH results in a carbonate error that corresponds to one type of systematic errors.
05. The slope of the calibration curve equation for the determination of Hg^{2+} in drinking water was $I = 0.30 \times [\text{Hg}^{2+}] + 0.40$, where I is a measure of the relative emission intensity, and the Hg^{2+} concentration is in nM. The reagent blank gave a value of 0.1 ± 0.012 . Which of the following statements is INCORRECT
- The detection limit of Hg^{2+} is 0.12 nM based on a signal-to-noise ratio of 3.
 - The concentration of Hg^{2+} in drinking water was 2 nM when the value of the relative emission intensity was 1.0.
 - The relative standard deviation for measuring the reagent blank is 0.12%
 - The calibration sensitivity is 0.30.
06. Which of the following statements concerning titration is INCORRECT?
- A titrimetric method based on the use of silver nitrate as titrant is sometimes named as argentometric titration.
 - If pH of a given weak acid at the half-titration point is 4.76, the K_a value of this weak acid is 1.75×10^{-5} .
 - In the titration of iodine with sodium thiosulfate, an addition of starch as an indicator is delayed until the color of the solution changes to pale yellow.
 - Titration of metal ions with EDTA in an $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer solution can enhance metal hydroxide from precipitating.

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07. Which of the following statements concerning amperometry and voltammetry is INCORRECT?
- In amperometry, we measure current as a function of a fixed potential between the working electrode and the reference electrode.
 - A gold electrode is usually used to oxidize analytes.
 - The current that we seek to measure in voltammetry is charging current.
 - The sensitivity for differential-pulse polarography is two to three orders of magnitude higher than for classical polarography.
08. Which of the following statements concerning potentiometry is INCORRECT?
- The two-electrode system is used for potentiometry measurements.
 - Potentiometric methods are performed by measuring the potential of electrochemical cells.
 - A pH meter is made of a glass membrane permeable to H^+ ions.
 - All potentiometric methods are insensitive to activity.
09. Which of the following statements concerning X-ray radiation is INCORRECT?
- X-Ray photoelectron spectroscopy can be used to measure the elemental composition of an analyte at part per billion range.
 - The Auger effect is involved in the analysis of energetic electrons that are ejected from atoms in response to a downward transition by another electron in the atom.
 - Auger electron spectroscopy is better for detecting chemical shifts than X-ray photoelectron spectroscopy.
 - An X-ray fluorescence instrument must have a source of high-energy X-rays.
10. Mass spectrometry is used heavily in different fields of chemistry to identify chemical species. Which of the following statements is NOT accurate:
- The molecule of interest is needed to be ionized in mass spectrometry.
 - The mass-to-charge ratio of an ion is measured in mass spectrometry.
 - The molecular mass of an ion can be determined by mass spectrometry.
 - Mass spectrometry can be used to measure electronic excitations in a molecule.
11. Which of the following statements concerning atomic spectroscopy is INCORRECT?
- In inductively coupled plasma atomic emission spectroscopy (ICP-AES), the species detected is a neutral atom or ion in an excited electronic state.
 - Atomic absorption spectroscopy is routinely used for simultaneous multi-element analysis.
 - Beam (or source) modulation is used in flame atomic absorption spectroscopy to eliminate interferences caused by emissions from the flame
 - Inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting most of the periodic table of elements.
12. Which of the following statements concerning matrix-assisted laser desorption ionization-time of flight-mass spectrometry (MALDI-TOF-MS) is INCORRECT?
- In the MALDI process, the matrix absorbs the laser light.
 - After absorbing light, the matrix is excited and transfers a proton to the analyte.
 - MALDI is classified as a soft ionization technique.
 - MALDI-TOF MS produces multi-charged ions.

背面有題

試題請隨卷繳回

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13. Which of the following detectors is the best for the analysis of $H_2(g)$ in gas chromatography?
- Flame ionization detector
 - Electron capture detector
 - UV-Visible absorbance detector
 - Thermal conductivity detector
14. Which of the following methods is the best for the separation of a mixture of Li^+ , Na^+ , and K^+ , and NH_4^+ in real-world samples?
- Ion-exchange chromatography
 - Ion-pair chromatography
 - Ion-exclusion chromatography
 - Ion-suppression chromatography
15. Which of the following statements concerning fluorescence is INCORRECT?
- The wavelength of the maximum fluorescence of an analyte was gradually red-shifted with increasing excitation wavelength.
 - The intensity of the fluorescence can be enhanced by increasing the excitation power.
 - Fluorescence lifetime tends to be shorter in a more polar environment.
 - The values of fluorescence quantum yield are between 0 and 1.

問答題 (每題四分)

16. Describe the strategies for detecting systematic errors in analytical experiments.
17. Describe how a fluoride selective electrode measures and the fluoride ion concentration.
18. List the variables that lead to band broadening in high performance liquid chromatography.
19. The Fourier Transform (FT) technique is used heavily in FT-infrared spectroscopy and FT-Raman instruments. Describe the FT instrumentation (i.e., Michelson interferometer).
20. How do pH and K_f (formation constant between EDTA and cation ions) affect the end point of an EDTA titration?

物理化學 (50%)

- 21.(10%) Treat the π electrons in benzene as particles freely moving over a circular ring of carbon atoms and calculate the minimum energy required for the excitation of a π electron. The carbon-carbon bond length in benzene is 140 pm. Energy levels of particle on ring $E_{m_l} = \frac{m_l^2 \hbar^2}{2I}$, $h = 6.62 \times 10^{-34}$ Js, mass of electron = 9.1×10^{-28} gram.

- 22.(10%) Suppose that in a reaction a substance A produces the desired compound B which goes on to decay to a worthless product C, each step of the reaction being first order. Calculate the greatest concentration of B in this reaction. The rate constant for A to B is k_a and the rate constant for B to C is k_b

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23.(10%) The equilibrium constant of the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ is 4.0×10^{24} at 300 K, 2.5×10^{10} at 500 K, and 3.0×10^4 at 700 K. Estimate the reaction enthalpy at 500.

24.(20%) Explain the following terms:

- (a) Hund's maximum multiplicity principle
- (b) Born Oppenheimer approximation
- (c) Clausius inequality
- (d) chemical potential
- (e) electronic configuration

國立中山大學 108 學年度 碩士暨碩士專班招生考試試題

科目名稱：有機化學及無機化學【化學系碩士班】

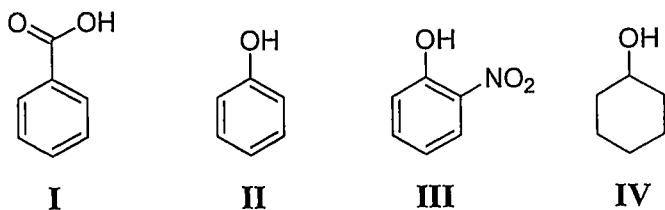
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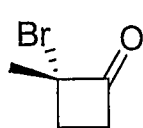
(一) 單選題 (2% × 29 = 58%)

1. Rank the following compounds in decreasing values of pKa (from highest to lowest).



- A) I > II > III > IV B) IV > III > II > I C) IV > II > III > I
D) III > I > II > IV E) I > III > II > IV

2. What is the IUPAC name for the following compound?

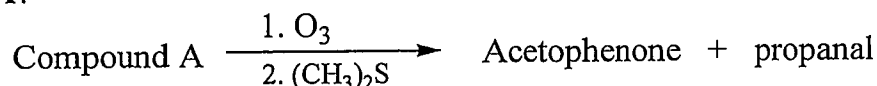


- A) (S)-2-methyl-2-bromobutanone
B) (S)-2-bromo-2-methylcyclobutanone
C) (R)-2-bromo-2-methylcyclobutanone
D) (S)-1-bromo-1-methyl-2-cyclobutanone
E) (R)-1-bromo-1-methyl-2-cyclobutanone

3. Of the species listed below, select those *less* basic than acetylide.

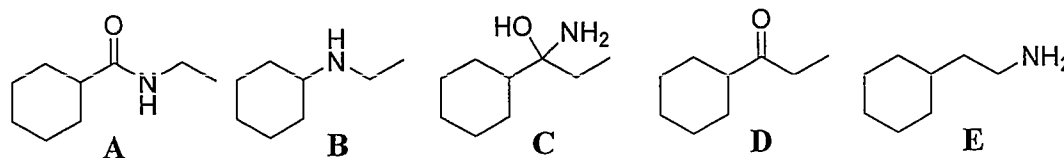
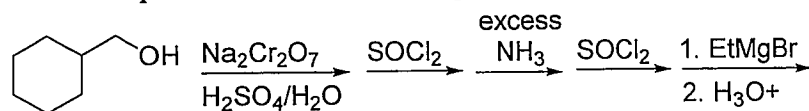
- A) BuLi B) NaNH₂ C) NaOCH₃ D) both A and C E) both B and C

4. **Compound A** on ozonolysis yields acetophenone and propanal. What is the structure of **compound A**?



- A) 2-phenyl-2-pentene B) 1-phenyl-1-hexene C) 1-phenyl-2-pentene
D) 2-phenyl-2-hexene E) none of the above

5. Predict the product for the following reaction sequence.



6. Provide the reagent(s) necessary to convert toluene to benzoic acid.

- A) 1. NBS, Δ; 2. NaOH B) 1. KMnO₄/NaOH/H₂O; 2. H₃O⁺ C) HNO₃/H₂SO₄
D) 1. CO₂; 2. H₃O⁺ E) none of the above

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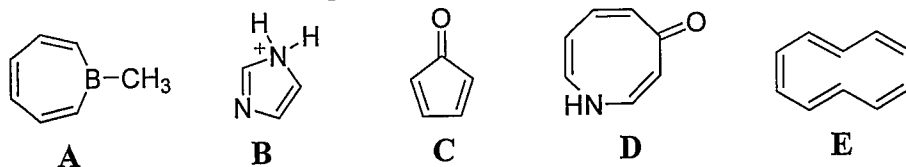
科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

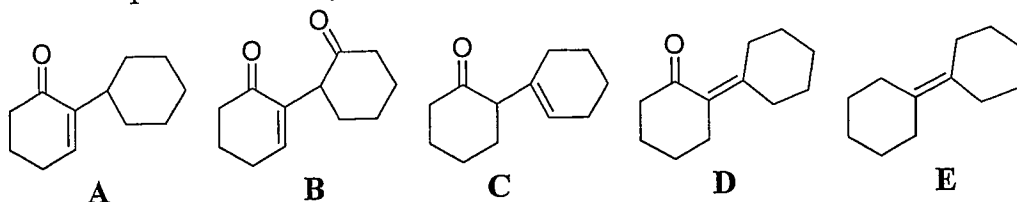
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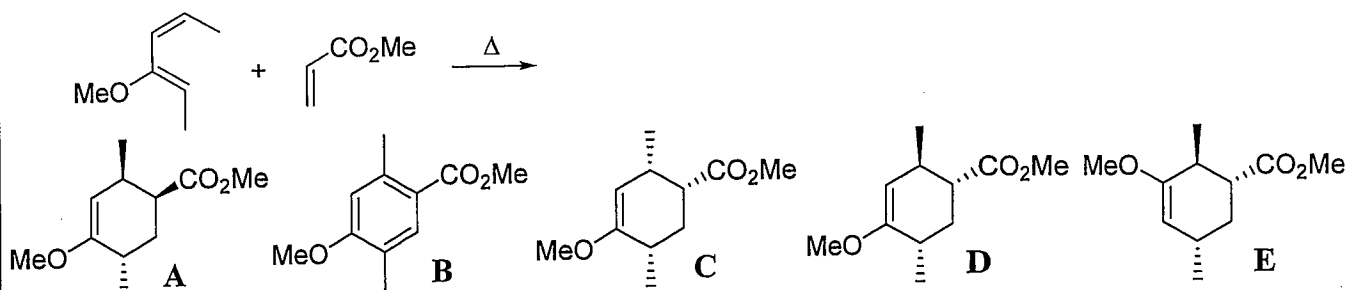
7. Which one of the following compound is aromatic?



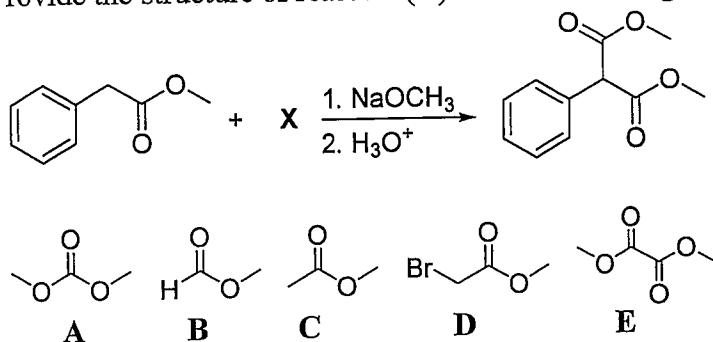
8. Predict the product when cyclohexanone reacts with aqueous sodium hydroxide at 100°C.



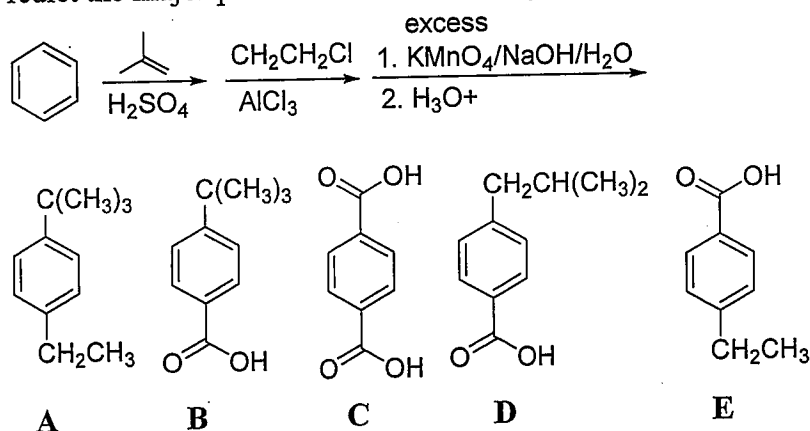
9. Give the major product for the reaction below.



10. Provide the structure of reactant (X) for the following reaction.



11. Predict the major product for the following reaction.



背面有題

試題請隨卷繳回

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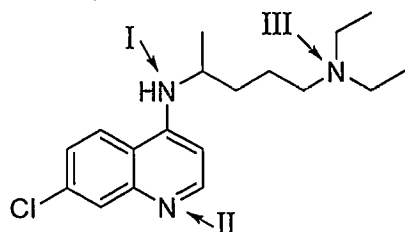
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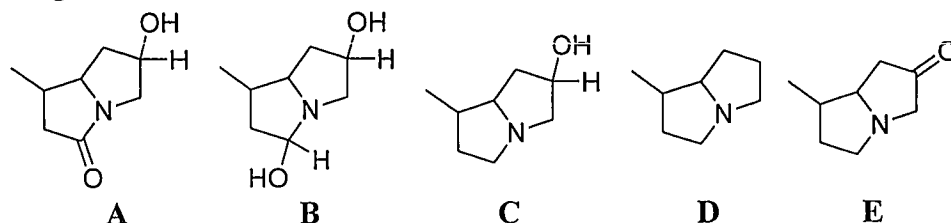
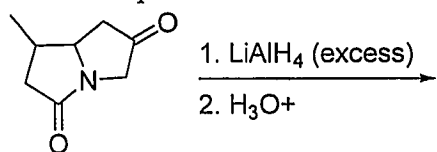
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12. Chloroquine is used as an antimalarial drug. Rank the three nitrogen atoms in decreasing (strongest to weakest) order of basicity.

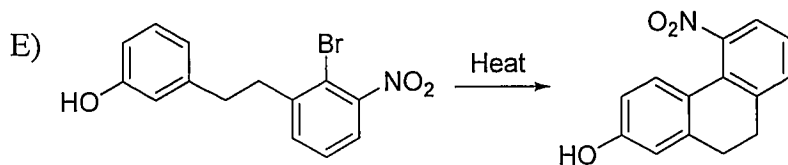
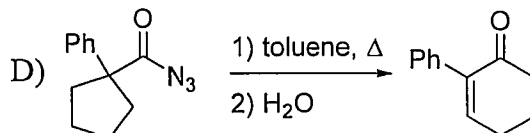
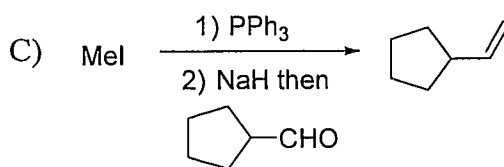
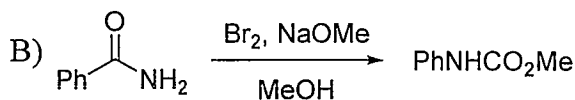
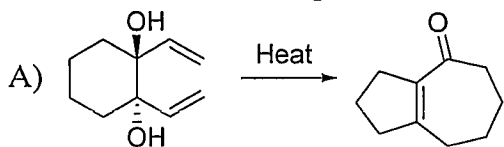


- A) III>I>II
 B) I>III>II
 C) II>I>III
 D) II>III>I
 E) III>II>I

13. Predict the product for the following reaction.



14. Which of the following reaction shown below give the WRONG product.



15. Choose the **correct** statement below:

- (A) μ^3 -CO has higher IR stretching frequency (ν) than terminal CO does.
 (B) The Ru-C distance of $\text{Ru}(\text{CE})_x$ complexes (E=O,S,Se,Te) is the shortest when E=oxygen.
 (C) Linear $\nu(\text{N-O})$ in neutral molecules is usually lower than bent $\nu(\text{N-O})$.
 (D) $\text{Ni}(\text{CO})_3(\text{PCl}_3)$ has higher CO stretching frequency than $\text{Ni}(\text{CO})_3(\text{PPh}_3)$
 (E) π -back bonding from CO will increase the $\nu(\text{CO})$ in metal carbonyl complexes

16. Which of the following specifies the **incorrect** magnetic moments for the complex?

- (A) 4.9 BM for $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (B) 2.8 BM for $[\text{Cr}(\text{CN})_6]^{4-}$
 (C) 5.9 BM for $[\text{Fe}(\text{CN})_6]^{3-}$ (D) 2.8 BM for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 (E) 1.7 BM for $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$

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17. Three separate solutions of $[M(H_2O)_6]^{2+}$ complexes ($M = Fe, Ni, \text{ and } Cu$) were mislabeled. In order to identify them, UV-Vis spectra were taken. Solution A has three ligand field bands. Solution B and C have only one band. Upon addition of excess CN^- , the single band of Solution B shifts to higher energy while that of Solution C becomes multiband. Which of the following is correct?
 (A) $M=Fe$ for Solution C (B) $M=Ni$ for Solution B (C) $M=Cu$ for Solution A
 (D) $M=Cu$ for Solution C (E) $M=Ni$ for Solution A
18. Choose the **correct** statement below:
 (A) Pure silicon is an insulator at room temperature
 (B) Metal has fully filled conduction band
 (C) Adding phosphorus in silicon makes an n-type semiconductor
 (D) Germanium is a p-type dopant for silicon semiconductor
 (E) Adding n-type dopant lowers the Fermi level
19. Which of the following name is **incorrect**?
 (A) dicyanotetrakis(methylisocyano)iron(II) for $[Fe(CN)_2(CH_3CN)_4]$
 (B) pentaamminenitridocobalt(III) sulfate for $[Co(N_3)(NH_3)_5]SO_4$
 (C) tris(2,2'-bipyridyl)nickel(II) bromide for $[Ni(bipy)_3]Br_2$
 (D) sodium tris(oxalato)vanadate(III) for $Na_3[V(C_2O_4)_3]$
 (E) potassium tetrachloroferrate(III) for $K[FeCl_4]$
20. The enthalpy change for a reaction can be obtained by:
 (A) slope from plot of $\ln K_{eq}$ vs. T (B) slope from plot of $\ln(1/K_{eq})$ vs. T
 (C) slope from plot of $\ln(1/K_{eq})$ vs. $1/T$ (D) slope from plot of $\ln K_{eq}$ vs. $1/T$
 (E) $-RT(\ln K_{eq})$
21. What is the bond order and magnetism for $Rh_2(\mu-CH_3COO)_4Cl_2$:
 (A) 3 bonds, paramagnetism (B) 2.5 bonds, paramagnetism
 (C) 3 bonds, diamagnetism (D) 1.5 bonds, paramagnetism
 (E) 2 bonds, paramagnetism
22. Which statement about the thiocyanate ion, SCN^- , is true?
 (A) Its Lewis structure contains an unpaired electron
 (B) Its shape is bent like that of H_2O
 (C) Only two correct resonance structures can be drawn
 (D) There are more than two sigma bonds in the ion
 (E) The formal charge on S can be +1, 0, -1
23. The predicted ligand dissociation rate ($L = \text{phosphine or phosphite}$) for
 $cis-Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L$ is
 (A) higher for PPh_3 than $P(n-Bu)_3$ (B) higher for PPh_3 than $P(p-CF_3C_6H_4)_3$
 (C) slower for PPh_3 than $P(OPh)_3$ (D) slower for PPh_3 than PMe_2Ph
 (E) None of the above
24. According selection rule, which of the following statement is **correct**?
 (A) $d \rightarrow d$ transition is forbidden because it is $u \rightarrow u$ symmetry
 (B) $s \rightarrow p$ transition is allowed because it is $u \rightarrow g$ symmetry
 (C) T_d complexes has stronger absorptions (ϵ coefficient) than that of Oh complexes
 (D) $\Delta S = \pm 1$ (E) $\Delta L = 0$

背面有題

試題請隨卷繳回

國立中山大學 108 學年度碩士暨碩士專班招生考試試題

科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

※本科目依簡章規定「不可以」使用計算機(混合題)

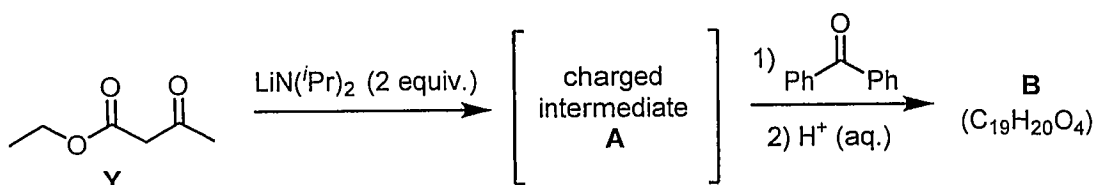
共 6 頁第 5 頁

25. Which electronic configuration for *Oh* geometry is not expected to have Jahn-Teller effect?
 (A) high spin d^4 (B) high spin d^9 (C) low spin d^7 (D) low spin d^5 (E) low spin d^6
26. Which compound can not be the metathesis product of $\text{MeCH}=\text{CHD}$ and $\text{MeCD}=\text{CHD}$?
 (A) $\text{CHD}=\text{CHD}$ (B) $\text{MeCH}=\text{CDMe}$ (C) $\text{MeCH}=\text{CHMe}$ (D) $\text{MeCH}=\text{CD}_2$ (E) $\text{MeCD}=\text{CDMe}$
27. Which of the following has the weakest bond?
 (A) S_2^+ (B) S_2 (C) S_2^- (D) O_2 (E) O_2^-
28. For Infrared spectra, which statement below is correct?
 (A) *trans*- $\text{Mo}(\text{CO})_2(\text{PMe}_3)_4$ has one CO IR active stretching signal
 (B) symmetric stretching of *cis*- $\text{Mo}(\text{CO})_2(\text{PMe}_3)_4$ is IR inactive
 (C) CO ligand has higher frequency than CN^- ligand
 (D) Terminal CO ligand usually has lower frequency than bent NO
 (E) *fac*- and *mer*- $\text{Mo}(\text{CO})_3(\text{PMe}_3)_3$ cannot be distinguished by IR
29. Choose the correct statement below:
 (A) F_2 has higher bond energy than Cl_2
 (B) $\text{Si}=\text{Si}$ bond is stronger than $\text{C}=\text{C}$ bond
 (C) Bond angle of NH_3 is larger than that of PH_3
 (D) SiO_2 forms single bond only while CO forms double bond.
 (E) The ground state of oxygen is singlet

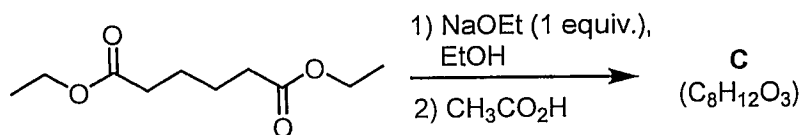
(二) 有機非選擇題 (22%)

1. Draw the structure for compound A, B, C, D, E, F and G with the correct stereochemistry where necessary. (2% × 7 = 14%)

a)



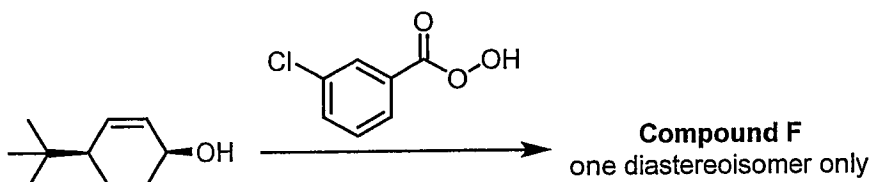
b)



c)



d)



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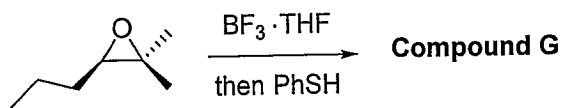
科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

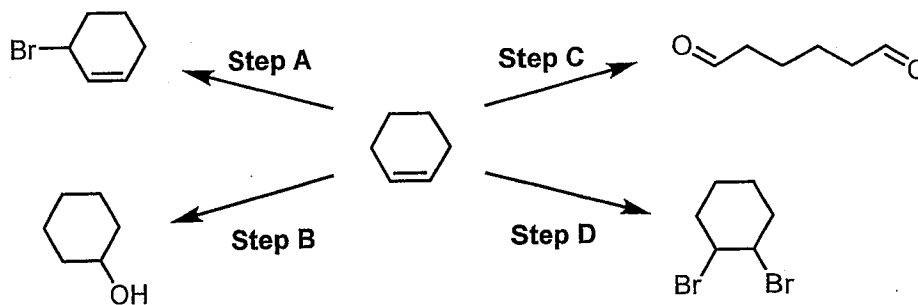
※本科目依簡章規定「不可以」使用計算機(混合題)

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e)



2. The scheme below shows some reactions of cyclohexene. Suggest appropriate reagents for **Step A**, **B**, **C** and **D** (more than one step may be required). (2% × 4 = 8%)



(三) 無機非選擇題 (20%)

1. Give point group for (a) $[\text{XeF}_5]^-$ anion, (b) NSF_3 , (c) P_4O_{10} (2% × 3 = 6%)
2. Explain why when blue CoCl_2 (in the form of $\text{Co}[\text{CoCl}_4]$) absorbs water and the color changed to pinkish red. (4%)
3. Identify the stereochemistry with Δ , Λ , δ , λ , α , β , *cis*, *trans*, *fac*, *mer* for the following structures. (2% × 5 = 10%)

