國立中山大學 110 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

- **考試開始鈴響前不得翻閱試題，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。**
- **違規者依本校招生考試試場規則及違規處理辦法處理。**

國立中山大學110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】　　題號：422002

※本科目依簡章規定「可以」使用計算機（廠牌、功能不拘）（混合題）　　

單擇題，每題兩分，共六十分

1. For an ideal gas in a perfect Carnot engine, which of the following processes can be used to do the greatest work?
   (A) Reversible adiabatic expansion (B) Reversible isothermal compression
   (C) Reversible adiabatic compression (D) Reversible isothermal expansion

2. In an adiabatic free expansion process for an ideal gas, which term is NOT zero?
   (A) ΔU (internal energy change) (B)W (Work) (C) ΔT (temperature change) (D)$\left(\frac{\partial U}{\partial V}\right)_T$

3. In Joule-Thomson experiment, which thermodynamic term is zero?
   (A) ΔH (Enthalpy change) (B) ΔU (internal energy change) (C) ΔV (Volume change) (D) ΔP (Pressure change)

4. What is the correct relationship between C_v and S?
   (A) $C_V = \left(\frac{\Delta S}{\Delta T}\right)_V$ (B) as dV=0, $dS = \frac{C_V}{T}dT$ (C) as dP=0, $dS = \frac{C_V}{T}dT$ (D)as dV=0, $dS = \frac{C_V}{T}dP$

5. If we mix 0.4 mole of pure benzene with 0.6 mole of pure toluene at temperature T. Assume this mixture is an ideal solution. What is ΔS?
   (A)0.4Rln0.4 + 0.6Rln0.6 (B) 0.4RTln0.4 + 0.6RTln0.6 (C) 0.4Rln0.6 + 0.6Rln0.4 (D) 0.4RTln0.6 + 0.6RTln0.4

6. What is the activity of 1 mole liquid water at 832.45 bar, 300 K?
   (A) 1.074 (B) 403.4 (C)1.822 (D)1.0007

7. How many wavenumbers (cm^{-1}) are equivalent to the energy at 300 Kelvin?
   (A) 100 cm^{-1} (B) 53 cm^{-1} (C) 0.371 cm^{-1} (D) 208 cm^{-1}

8. What is the boundary conditions for a "particle in a box" model?
   (A) $\psi(0) = \psi(L) = 0$ (B)$\psi(0) = \psi(L) = \infty$ (C) $\psi(0) = \psi(L) = 1$ (D) $\psi(0) = 0, \psi(L) = \infty$

9. If a potential function of a diatomic molecule can be described by a Morse potential, $V(x) = D_e(1 - e^{-\beta x})^2$, what is the force constant k?
   (A) βD_e (B) $1/2\,\beta De$ (C) $1/2\,\beta^2 D_e^2$ (D) $2\,\beta^2 D_e$

10. The $Y_1^1(\theta, \phi)$ is an eigenfunction of $\hat{L}^2$, so what is the eigenvalue?
    (A) $2\hbar$ (B) $2\hbar^2$ (C) $\hbar^2$ (D) 1

11. What is the ground state term of molecular oxygen?
    (A)^3P (B)$^3\Sigma_g^-$ (C) $^1\Sigma_g^+$ (D) $^3\Pi$

12. To measure a correct rate coefficient, which order reaction does not require to know the absolute concentrations of reactants?
    (A) 1st order (B) 2nd order (C) 0th order (D) 3rd order

13. If the population decay channels of the excited state decay include three channels, such as fluorescence channel (k_F), internal conversion channel (k_{IC}), and intersystem crossing channel (k_{ISC}), what is the observed fluorescence lifetime τ_F?
(A)1/ k_F (B) 1/ $(k_F + k_{IC})$ (C) 1/ $(k_F + k_{IC} + k_{ISC})$ (D) 1/ $(k_F + k_{ISC})$

14. The rate constant for the reaction of $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$ is 1.22×10^{-6} $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at 575 K and 2.50×10^{-6} $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at 716 K. Estimate the value of E_a from these data. (Assuming the E_a and pre-exponential factor are temperature independent)
(A)185 $kJmol^{-1}$ (B) 158 $kJmol^{-1}$ (C) 116 $kJmol^{-1}$ (D) 161 $kJmol^{-1}$

15. In statistical thermodynamics, which kind of molecular motion has greatest contribution to the entropy?
(A) Rotation (B) Vibration (C)Translation (D)electronic transition

16. If we compare two means from two samples, which test do we use?
(A) t-test
(B) F-test
(C) Q-test
(D) R-test

17. Which of the following statements are **INCORRECT**?
(A) 100 ppb Hg^{2+} = 0.1 ppm Hg^{2+}
(B) The number 1.2500×10^4 has five significant figures.
(C) 0.02 (±0.02) + 0.01 (±0.02) − 0.02 (±0.03) = 0.01 (± 0.04)
(D) Molality is the number of moles of a substance per liter of solution.

18. Which of the following statements concerning the detection of Random error are **INCORRECT**?
(A) Random error is also called an indeterminate error.
(B) Random error has a Gaussian normal distribution.
(C) Random error is always present in a measurement.
(D) Random error can be reduced by decreasing the number of measurements

19. The calibration curve equation for quantifying Cu^{2+} standard was I = 51.00 × $[Cu^{2+}]$ + 1.00, where I is the intensity and the Cu^{2+} concentration is in micromole/L. The reagent blank, measured by three repeated experiments, gave a value of 0.30 ± 0.04. What is the detection limit for Cu^{2+} based on a signal-to-noise ratio of 2?
(A) 1.56 nM.
(B) 1.35 nM.
(C) 2.56 nM.
(D) 2.35 nM.

20. Which of the following statements concerning titration are **INCORRECT**?
(A) The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid.
(B) The pK_a values of a diprotic acid H_2A are pK_{a1} = 3.00, pK_{a2} = 8.00. At pH 9.00, the major species are A^{2-}
(C) The equivalent volume for titrating 50.00 mL of a solution (0.05 M in iodide ions and 0.08 M in chloride ions) with 0.1 M silver nitrate is 60 mL.
(D) In EDTA titration, ammonia often is required to prevent the precipitation of metal ions.

21. Which of the following statements concerning voltammetry are **INCORRECT**?

(A) The working electrode carries out the electrochemical even of interest.
(B) The progressive scanning of carbon electrodes is extended to more negative potentials than platinum or gold electrodes.
(C) A sharp peak profile for each species is observed in differential pulse voltammetry
(D) A charging current results from redox reactions at the working electrode and the auxiliary electrodes.

22. Which of the following statements concerning capillary electrophoresis are **INCORRECT**?
(A) Micellar electrokinetic chromatography is based on the addition to the buffer solution of a micellar "pseudo-stationary" phase.
(B) Capillary zone electrophoresis allows uncharged analytes to be separated.
(C) The intrinsically low flow-rate of capillary electrophoresis is advantageous to connect with electrospray ionization-mass spectrometry.
(D) The electroosmotic flow remains almost constant with an increase in electric field strength.

23. Which of the following statements concerning surface spectroscopic methods are **INCORRECT**?
(A) X-ray photoelectron spectroscopy is useful to identify the elemental composition of the sample and determine its valance state.
(B) The elemental hydrogen in the sample can be detected by X-Ray photoelectron spectroscopy.
(C) The process of Auger electron spectroscopy (AES) includes atomic ionization, electron emission, and analysis of the emitted Auger electrons
(D) In X-Ray photoelectron spectroscopy, detection limits for most of the elements are in the parts per thousand range.

24. Which of the following statements concerning inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass-spectrometry (ICP-MS) are **INCORRECT**?
(A) ICP-OES can be used to analyze isotopes of elements
(B) ICP-MS is more sensitive than ICP-OES
(C) The steps associated with ICP-MS analysis of the samples include introduction-atomizing, ionization, mass separation, and detection
(D) ICP-OES and ICP-MS both provide high throughput multi-element analysis.

25. The activity coefficients of H^+ and OH^- are 0.83 and 0.76 when the ionic strength is 0.1. The pH of water containing 0.10 M $LiNO_3$ at 25°C are
(A) 6.98
(B) 7.00.
(C) 7.02
(D) 7.04

26. Which of the following statements concerning gas chromatography (GC) are **INCORRECT**?
(A) The split injection is selected when the concentration of the target analyte in the sample is at trace level.
(B) GC combined with a flame-ionization detector is used extensively for the detection of hydrocarbons.
(C) GC in conjugation with a thermal-conductivity detector is useful for the analysis of a mixture of gases
(D) A polydimethylsiloxane-based polymer is heavily used as a stationary phase in GC.

27. Which of the following methods concerning high-performance liquid chromatography (HPLC) are **INCORRECT**?
   (A) Ion-pair chromatography is powerful for the separation of metal ions due to the addition of ion-pair reagents.
   (B) Size-exclusion chromatography is useful for the separation of large-sized macromolecules, but it suffers from limited resolution and long analysis time
   (C) In reversed-phase HPLC, polar analytes elute earlier than nonpolar ones.
   (D) In ion-exchange chromatography, ion exchangers bind preferably ions of higher charge and increased hydrated radius

28. Which of the following methods concerning absorption are **INCORRECT**?
   (A) UV-Visible spectroscopy of organic compounds is usually associated with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$
   (B) The intensity of absorbance is proportional to the log of the absorbing species concentration
   (C) An atomic absorption spectrum consists of a series of line peaks
   (D) X-ray absorption spectroscopy (XAS) can probe the chemical surroundings around an atom of interest.

29. Which of the following statements concerning fluorescence are **INCORRECT**?
   (A) The lifetime of fluorescence is 10^{-8} to 10^{-4} s.
   (B) The difference between the excitation and emission wavelengths is called the Stokes Shift.
   (C) Fluorescence intensity is sensitive to environmental factors, such as pH and solvent polarity.
   (D) The fluorescent quantum yield is dependent of excitation intensity.

30. Which of the following statements concerning gravimetric methods are **INCORRECT?**
   (A) The particle size of a precipitate can be enhanced by minimizing the relative super-saturation during precipitate formation
   (B) An electric double layer consists of the primary adsorption layer and counter-ion layer.
   (C) Peptization is a process in which a precipitate is heated in the mother liquor.
   (D) A gravimetric volatilization method is the classical method for the determination of hydrogen and carbon in organic compounds

問答題，共四十分

31. (10%) Please derive the following equations:
   (a) $\left(\frac{\partial U}{\partial T}\right)_P = C_P - PV\beta, (\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P)$
   (b) $C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$

32. (10%) The activation energy E_a can be defined from the Arrhenius expression as

$$E_a = kT^2 \frac{\partial \ln k(T)}{\partial T}$$

Use the equation $k(T) = \pi b_{max}^2 \nu_r \exp(-\frac{\varepsilon^*}{kT})$ to show that

$$E_a = \frac{1}{2}kT + \varepsilon^*$$

33. (4%) Standard addition is especially appropriate when matrix effect present. Explain how the analytical signal is affected by matrix effect. And, What is the most important assumption in the standard addition method?

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34. (4%) We have different mass analyzers, including time-of-flight, triple-quadrupole, and linear ion trap. When we use each of them?

35. (4%) Describe the working principle of Fluoride ion-selective electrode.

36. (4%) Describe the variables that cause the band broadening in gas chromatography, high-performance chromatography, and capillary electrophoresis.

37. (4%) For CO_2, all vibrational modes that are Raman active are IR inactive and vice-versa. For N_2O, the vibrational modes are both Raman and infrared active. What is the effect of such a phenomenon?

國立中山大學110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】

—作答注意事項—

考試時間：100分鐘

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國立中山大學110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

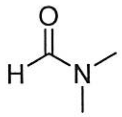
※本科目依簡章規定「不可以」使用計算機(混合題)　　

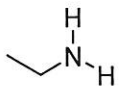
一、單選題（54%）

第1～12題，每題1分

1. A student synthesized Vitamin C and got a pair of enantiomers (*d*- and *l*-ascorbic acid). The specific optical of the synthesized Vitamin C is +10°. What is the percentage of *l*-ascorbic acid in the synthesized Vitamin C, given that the specific rotation of *l* -ascorbic acid: $[\alpha]_D^{25}$ +20°?
(A) 100% (B) 25% (C) 50% (D) 75% (E) 0%

2. Which of the following is an aprotic solvent?


(A)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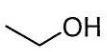
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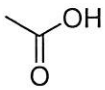
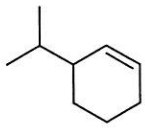
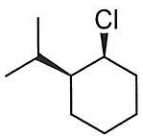
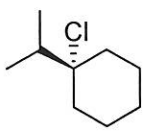

(D)


(E)

3. Which of the following alkyl chlorides would afford the indicated product upon reaction with NaOH?




(A)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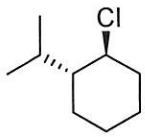
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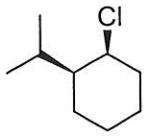
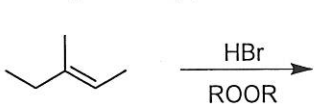
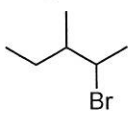

(D)

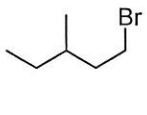
4. Which of the following alkene addition reactions undergoes *anti* addition?
(A) hydroboration-oxidation
(B) catalytic hydrogenation (H_2, Pt)
(C) dihydroxylation of OsO_4 (catalytic) and NMO
(D) addition of Br_2

5. Which of the bases below would result in the most complete deprotonation of a terminal alkyne?
(A) $NaNH_2$
(B) NH_3
(C) NaOH
(D) $NaOCH_2CH_3$
(E) KOH

6. Predict the product(s) of the following reaction?




(A)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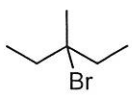
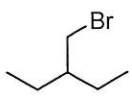
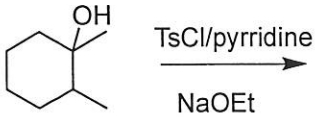
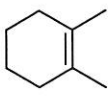
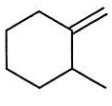

(C)

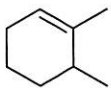

(D)

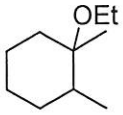
7. The major product for the following reaction:



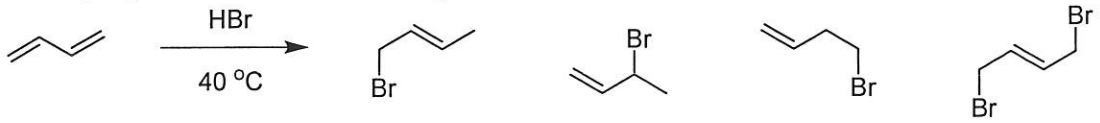

(A)


(B)


(C)


(D)

8. Predict the major product for the following reaction:



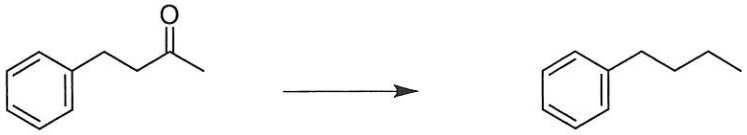
(A)　(B)　(C)　(D)

9. Which one of the following compounds is aromatic?

(A)　(B)　(C)　(D)

10. Compared to Friedel-Crafts acylation, the disadvantage(s) of Friedel-Crafts alkylation is/are:
(A) rearrangement
(B) polyalkylations
(C) the same
(D) (A) and (B)

11. Which of the following reagents could not be used to carry out the following transformation?



(A) Zn(Hg), HCl
(B) $LiAlH_4$, ether
(C) $HSCH_2CH_2SH$, BF_3; then Raney Ni (H_2)
(D) 1. NH_2NH_2/H^+ 2. KOH/H_2O/heat

12. The reactivity towards nucleophilic substitution of carboxylic acid derivatives in decreasing order (most to least).
(A) acid anhydride > acyl chloride > ester > amide
(B) acid anhydride > acyl chloride > amide > ester
(C) acyl chloride > acid anhydride > amide > ester
(D) acid anhydride > amide > acyl chloride > ester
(E) acyl chloride >acid anhydride > ester > amide

第 13～33 題，每題 2 分

13. The complementary color of yellow is (A) red (B) orange (C) green (D) blue (E) violet

14. Which of the following has the largest ionic radius? (A) O^{2-} (B) F^- (C) Na^+ (D) Mg^{2+} (E) Al^{3+}

15. Which of the following has the largest bond angle? (A) H_2O (B) H_2S (C) H_2Se (D) H_2Te (E) these molecules have the same bond angle

16. Which is a Lewis acid? (A) BF_3 (B) CF_4 (C) NF_3 (D) OF_2 (E) F_2

17. Which is a π-donor? (A) BeH_2 (B) BH_3 (C) CH_4 (D) NH_3 (E) OH_2

18. Which of the following is non-polar? (A) $PFCl_4$ (B) PF_2Cl_3 (C) PF_3Cl_2 (D) PF_4Cl (E) none of the above

19. The point group of $Ni(CO)_4$ is (A) C_{2v} (B) C_{2h} (C) D_{4d} (D) D_{4h} (E) T_d

20. Trien is a linear tetradentate polyamine. Which one is achiral? (A) $[\alpha\text{-Co(trien)Cl}_2]^+$ (B) $[\beta\text{-Co(trien)Cl}_2]^+$ (C) $[\gamma\text{-Co(trien)Cl}_2]^+$ (D) $[\text{trans-Co(trien)Cl}_2]^+$ (E) none of the above

21. Among H, Ar, and Fe in their ground state electron configurations, which has 3d orbitals? (A) only H (B) only Ar (C) only Fe (D) only Ar and Fe (E) H, Ar, and Fe

22. What is the ground state electron configuration of Mn^{2+}? (A) $[Ar]4s^23d^3$ (B) $[Ar]4s^24d^3$ (C) $[Ar]4s^13d^4$ (D) $[Ar]4s^14d^4$ (E) $[Ar]3d^5$

23. The ground term of electron configuration of $[Cu(NH_3)_4]^{2+}$ is (A) ${}^1A_{1g}$ (B) ${}^2T_2$ (C) ${}^2E$ (D) ${}^2T_{2g}$ (E) ${}^2E_g$

24. The wave function for an orbital is expressed as $\psi = (1/3)^4(2/\pi)^{1/2}(Z/a_0)^{3/2}(\cos\theta)(6\sigma-\sigma^2)\exp(-\sigma/3)$; where $\sigma = Z\cdot r/a_0$ and $a_0 = 0.529$ Å. What is this orbital? (A) 2s (B) $2p_x$ (C) $3p_z$ (D) $3d_{xy}$ (E) none of the above

25. Which has a bond order of 1.5? (A) N_2^+ (B) O_2^+ (C) F_2^+ (D) Ne_2^+ (E) none of the above

26. In $Mo(CO)_6$, the σ interaction (in unit of e_σ) of $4d_{x2-y2}$ with one CO lying on the xy plane is (A) 0 (B) 1/4 (C) 1/3 (D) 3/4 (E) 1

27. In $Mo(CO)_6$, the π interaction (in unit of e_π) of $4d_{x2-y2}$ with one CO lying on the xy plane is (A) 0 (B) 1/4 (C) 1/3 (D) 3/4 (E) 1

28. The ligand field stabilization energy (in unit of Δ_o) of $[Co(OH_2)_6]^{3+}$ is (A) 0 (B) –0.4 (C) –0.6 (D) –2.4 (E) none of the above

29. The HOMO of $[Ni(CN)_4]^{2-}$ is (A) only $3d_{x2-y2}$ (B) only $3d_{z2}$ (C) $3d_{x2-y2}$ and $3d_{z2}$ (D) $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ (E) $3d_{x2-y2}$, $3d_{z2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$

30. $[V(OH_2)_6]^{3+}$ has a magnetic moment (in Bohr magneton) of (A) 0 (B) 0.7 (C) 1.4 (D) 2.8 (E) 3.5

31. Which of the following shows the strongest Jahn-Teller effect? (A) $[Ti(OH_2)_6]^{3+}$ (B) $[V(OH_2)_6]^{3+}$ (C) $[Cr(OH_2)_6]^{3+}$ (D) $[Mn(OH_2)_6]^{3+}$ (E) $[Fe(OH_2)_6]^{3+}$

32. In UV-vis spectroscopy, CrO_4^{2-} gives absorption bands of (A) only d-d transition (B) only LMCT (C) only MLCT (D) all of the above (E) LMCT and MLCT

33. The valence electron count of VMe_5 is (A) 10 (B) 12 (C) 14 (D) 16 (E) 18

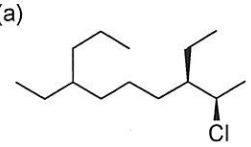
國立中山大學 110 學年度碩士暨碩士專班招生考試試題

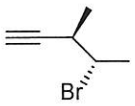
科目名稱：有機化學及無機化學【化學系碩士班】　　題號：422001

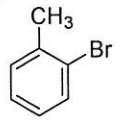
※本科目依簡章規定「不可以」使用計算機(混合題)　　

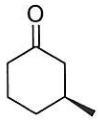
二、非選擇題（46%）

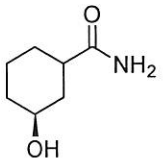
1. Assign a systematic name for each of the following compounds: (5%)

(a) 

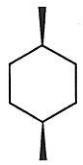
(b) 

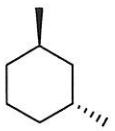
(c) 

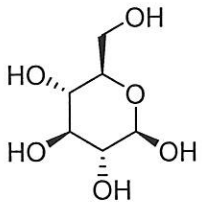
(d) 

(e) 

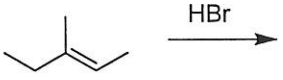
2. Draw both chair conformations for each of the following compounds, and identify the more stable chair conformation: (6%)

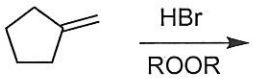
(a) 

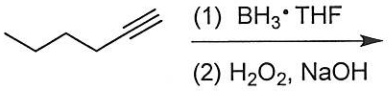
(b) 

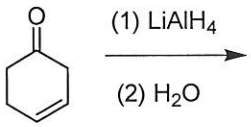
(c) 

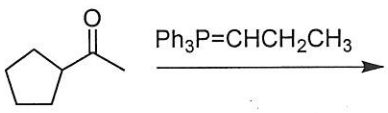
3. Draw the major product for each of the following reactions: (8%)

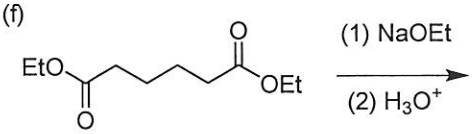
(a) 

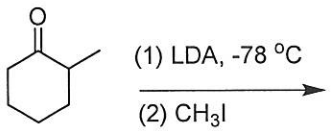
(b) 

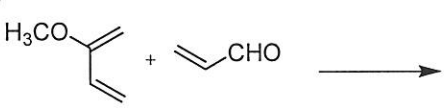
(c) 

(d) 

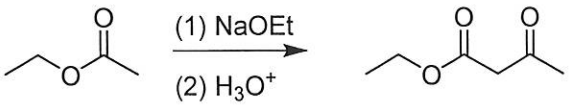
(e) 

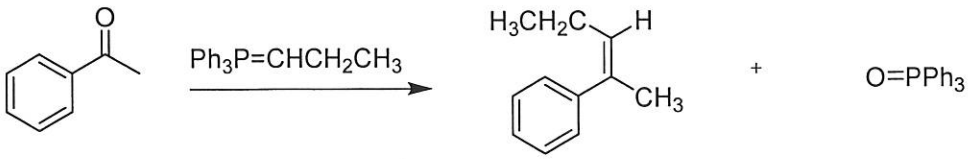
(f) 

(g) 

(h) 

4. Write the reaction mechanism of the following reactions: (10%)

(a) 

(b) 

國立中山大學110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

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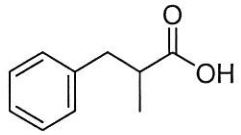
5. Design a synthesis of 3-propylaniline from benzene. (5%)

6. The synthesis of the following compound using malonic ester synthesis. (4%)



7. Draw the structures of all possible metathesis products of propene with 1-butene. (8%)