國立中山大學 101 學年度碩士暨碩士專班招生考試試題

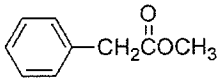
科目：有機化學及無機化學【化學系碩士班】

題號：4043

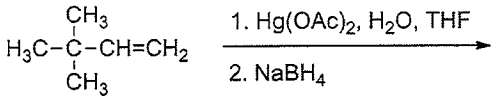
單選題 (2% × 31 = 62%)

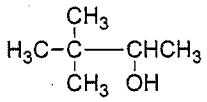
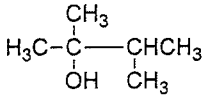
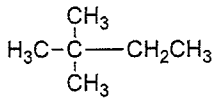
1. Which of the following esters can not produce Claisen condensation product?

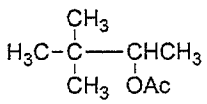
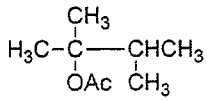
(A) $CH_3CH_2CH_2COCH_3$ (B) $CH_3CHCH_2COCH_3$ (CH_3) (C) $CH_3CHCOCH_3$ (CH_3)

(D)  (E) $CH_3COCH_2CH_3$

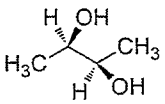
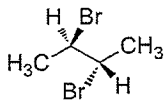
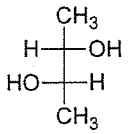
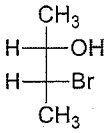
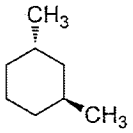
2. What is the major product of the following reaction?



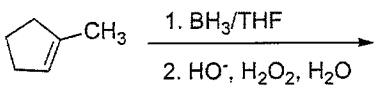
(A)  (B)  (C) 

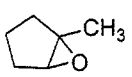
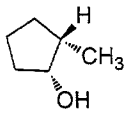
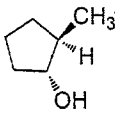
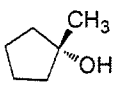
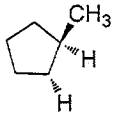
(D)  (E) 

3. Which of the following compounds is a *meso* compound?

(A)  (B)  (C)  (D)  (E) 

4. What is the major product of the following reaction?

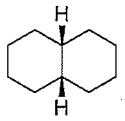


(A)  (B)  (C)  (D)  (E) 

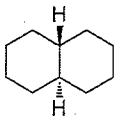
5. Which of the following anions is the strogest Bronsted base?

(A) H^- (B) $^-CH_3$ (C) $^-NH_2$ (D) ^-OH (E) F^-

6. *cis*-Decalin is less stable than *trans*-decalin. Assume that the 1,3-diaxial interactions in *cis*-decalin are similar to those in axial methylcyclohexane [that is, one CH_2 and H interaction costs 0.9 kcal/mol], and what is the energy difference between *cis*- and *trans*-decalin.



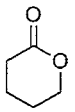
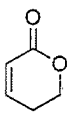
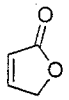
cis-decalin



trans-decalin

(A) 0.9 kcal/mol (B) 1.8 kcal/mol (C) 2.7 kcal/mol (D) 3.6 kcal/mol (E) 4.5 kcal/mol

7. Which of the following lactones shows the highest C=O stretching absorption frequency?

(A)  (B)  (C)  (D)  (E) 

8. Which of the following substituents should be assigned as the highest priority according to the Cahn-Ingold-Prelog sequence rule?

(A) $-CH=CH_2$ (B) $-CN$ (C) $-CH_2NH_2$ (D) $-CH_2Br$ (E) $-CO_2H$

9. When electron-impact ionozation is used, the Mass spectrum of 2,2-dimethylpropane shows many fragment ions. Which of the following would you expect to be the base peak?

(A) m/z = 15 (B) m/z = 29 (C) m/z = 41 (D) m/z = 57 (E) m/z = 72

10. Which of the following nucleophiles is most reactive toward CH_3I in methanol?

(A) CH_3O^- (B) NH_3 (C) F^- (D) Br^- (E) CH_3S^-

11. The fragment $Ru(CO)_3$ is isolobal with: (A) CH (B) CH_2 (C) BH (D) BH_2 (E) NH.

12. Pick the complex having Jahn-Teller effect: (A) $Fe(OH_2)_6^{2+}$ (B) $Co(OH_2)_6^{2+}$ (C) $Ni(OH_2)_6^{2+}$ (D) $Cu(OH_2)_6^{+}$ (E) $Zn(OH_2)_6^{2+}$.

13. Pick the lowest C-O stretching frequency: (A) $Ti(CO)_6^{2-}$ (B) $V(CO)_6^{-}$ (C) $Cr(CO)_6$ (D) $Mn(CO)_6^{+}$ (E) $Fe(CO)_6^{2+}$.

14. Determine the number of IR-active O-H stretching bands for H_3O^+: (A) 0 (B) 1 (C) 2 (D) 3 (E) 4.

15. The point group of tungsten hexahydride is: (A) O_h (B) T_d (C) C_{2v} (D) C_3 (E) none of the above.

16. Pick the molecule having C_{2v} symmetry: (A) PCl_5 (B) $PFCl_4$ (C) PF_2Cl_3 (D) PF_3Cl_2 (E) PF_3.

17. For a hydrogen atom, assuming its 2p orbital energy is E, estimate its 5d orbital energy: (A) 5E/2 (B) 2E/5 (C) 25E/4 (D) 4E/25 (E) none of the above.

18. Pick the molecule or ion that is chiral: (A) OH^- (B) H_2O (C) H_2O_2 (D) H_3O^+ (E) none of the above.

19. Pick the ion that is diamagnetic: (A) O_2^- (B) O_2^{2-} (C) N_2^- (D) N_2^{2-} (E) N_2^{3-}.
20. Estimate the spin-only magnetic moment (in B.M.) of $Os(OH_2)_6^{3+}$: (A) 0 (B) 1.41 (C) 1.73 (D) 2.83 (E) none of the above.
21. Determine the ground-state free-ion term for $Ni(OH_2)_6^{2+}$: (A) $^3F_4$ (B) $^3F_2$ (C) $^3D_4$ (D) $^3D_2$ (E) none of the above.
22. Pick the most labile compound in the following: (A) $Mn(\eta^5\text{-}C_5H_5)_2$ (B) $Fe(\eta^5\text{-}C_5H_5)_2$ (C) $Co(\eta^5\text{-}C_5H_5)_2$ (D) $Ni(\eta^5\text{-}C_5H_5)_2$ (E) they are equally stable.
23. Pick the highest Re-Re bond order in the following: (A) $[Re_2Cl_4(PMe_2Ph)_4]$ (B) $[Re_2Cl_4(PMe_2Ph)_4]^+$ (C) $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$ (D) $[Re_2Cl_4(PMe_2Ph)_4]^{3+}$ (E) they all have the same Re-Re bond order.
24. Pick the fragment that is isolobal with phosphorus: (A) $Pd(CO)_3$ (B) $PtCl_3^-$ (C) $Re(CO)_4$ (D) $Fe(\eta^5\text{-}C_5H_5)(CO)_2$ (E) $Ni(\eta^5\text{-}C_5H_5)$.
25. Determine the number of framework orbitals for B_8H_{16}: (A) 11 (B) 12 (C) 13 (D) 14 (E) 15.
26. Pick the strongest base from the following in reactions with trimethylboron: (A) pyridine (B) 2-methylpyridine (C) 4-methylpyridine (D) 2-*tert*-butylpyridine (E) 4-*tert*-butylpyridine.
27. Pick the highest emission frequencies for ZnSe quantum dots with the following diameters (in nm): (A) 10 (B) 30 (C) 50 (D) 100 (E) they all have identical emission frequencies.
28. Where distinguishable, pick the strongest acid from the following: (A) HF (B) H_2SO_3 (C) H_2SO_4 (D) $HClO_4$ (E) HSO_3F.
29. Schrock carbenes are characteristic of (A) containing late transition metals (B) containing metals with lowest possible oxidation states (C) containing β-heteroatoms (D) containing nucleophilic α-carbon (E) containing nucleophilic α-hydrogen.
30. Assuming the ionization energy of a hydrogen atom is E, estimate the 4f orbital energy for a Li^{2+} cation: (A) 3E/4 (B) –3E/4 (C) 9E/16 (D) –9E/16 (E) E/4.
31. The electron count of tungsten hexamethyl is: (A) 12 (B) 14 (C) 16 (D) 18 (E) 20.

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題號：4043

非選擇題 (38%)

I. Reactivity and Statement (2% × 4 = 8%):

(a) Give the formula of all products from the reaction of $Mn(CO)_5(Me)$ with CO.

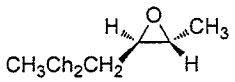
(b) Give the formula of all products from the thermolysis reaction of $Ta(CH_2CMe_3)_5$.

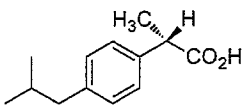
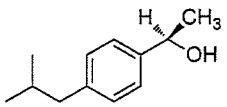
(c) Explain briefly why two separate water exchange rates are found for $[Cu(H_2O)_6]^{+2}$ in aqueous solution.

(d) Explain briefly why CO and N_2 are isoelectronic but exhibit dramatically different reactivity. Which one is more reactive?

II. Synthesis questions. (5% x 2 = 10%)

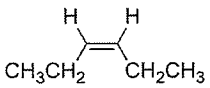
How would you prepare the following compounds from the given starting materials? More than one step may be required. Also indicate clearly all the other common reagents needed for the transformation in each step.

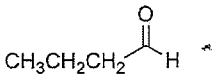
(a)  from HC≡CH

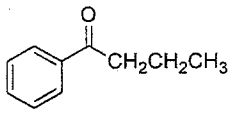
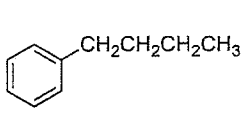
(b)  from 

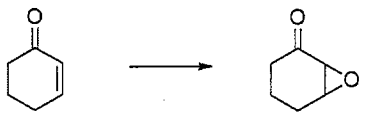
III. Reagent questions. (3% x 5 = 15%)

What reagents would you use to accpmplish each the following transformation?

(a) $CH_3CH_2C{\equiv}CCH_2CH_3$ ⟶ 

(b) $CH_3CH_2CH_2CH_2OH$ ⟶ 

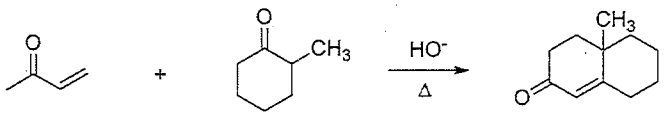
(c)  ⟶ 

(d) 

(e) 

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

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



Physical Chemistry (50%)

Notice:

You may choose to solve any 5 of the 6 problems given below.

The physical constants and formula you may need are listed as follows:

Avogadro constant $N_A = 6.022\times10^{23}$

Boltzmann constant $k_B = 1.38\times10^{-23}$ J/K

Planck constant $h = 6.626\times10^{-34}$ Js, $\hbar=h/2\pi = 1.055\times10^{-34}$ Js

Electron charge $e = 1.602\times10^{-19}$ C

Electron mass $m_e = 9.11\times10^{-31}$ kg

Proton mass $m_p = 1.67\times10^{-27}$ kg

Speed of light in vacuum $c = 2.998\times10^{8}$ m/s

Differential expressions of internal energy, enthalpy and free energies:

$dU = TdS - pdV$

$dH = TdS + Vdp$

$dG = -SdT + Vdp$

$dA = -SdT - pdV$

Translational, rotational and vibrational partition functions:

$$q_{trans} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}V, q_{rot} = \left(\frac{8\pi^2 mk_BT}{h^2}\right)^{3/2}\frac{(\pi I_A I_B I_C)^{1/2}}{\sigma}, q_{vib} = (1-e^{-h\nu/k_BT})$$

The character table of point group C_{2v}

	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1		-1
B_2	1	-1	-1	1

The irreducible decomposition of point group representation:

$$a_i = \frac{1}{g}\sum_{\text{all classes}} n_R\chi_i(R)\chi(R)$$

1. Consider the following chemical reaction $A+B \rightleftharpoons C+D$. Given the standard free energies of formation and standard entropies:

	A	B	C	D
G_f° (kJ/mol)	220	240	300	180
S_f° (J/mol/K	142	157	176	153

(i) Which reaction, the forward or backward reaction, is endothermic?
(ii) Calculate the equilibrium constant K of forward reaction at 298 K.
(iii) Which reaction, the forward or backward reaction, is spontaneous at 298 K?
(4+3+3 pts)

2. (i) What is the most important feature of colligative properties? (ii) Explain why colligative properties are a consequence of entropy. (iii) Give at least one practical application of colligative properties. (3 + 4 + 3 pts)

3. We may assume that the surface water is a monolayer with O-O distance between two closest water molecules being 298 pm. The measured hydrogen bond energy of water is 7.9 kJ/mol. The surface tension of water measured at 25 °C is 0.072 N/m. (i) Is the energy of water molecule on surface higher or lower than that of water molecule in bulk? (ii) Calculate the energy difference between a water molecule in the bulk and that on the surface. (iii) Is it reasonable to hypothesize that about half of hydrogen bonds are broken on the surface? (2+6+2 pts)

4. The lowest energy atomic absorption line of He^+ ions is at a photon energy of 40.814 eV, while that of atomic H atoms is at 10.197 eV. (i) Give the configurations and term symbols for the states involved in the transitions. (ii) Explain why the ratio of photon energies is very close to four but not exactly four. (iii) Explain why at higher resolution the 40.814 eV spectral line is a doublet. (iv) How many lines can be observed at the 40.814 eV spectral line when He^+ ions are in a strong magnetic field? (3+2+2+3 pts)

5. Given the symmetry group of water C_{2v}, (i) Write, in terms of matrix, the symmetry operations of the point group on the translational motion of water. (ii) Write, in terms of matrix, the symmetry operations of the point group on the rotational motion of water. (iii) Calculate the symmetry species of the normal modes of vibration. (3+3+4 pts)

6. A bimolecular elementary reaction $A+B \rightleftharpoons A\cdots B$ occurs at 300 K in a fixed volume and can be regarded as in equilibrium. Suppose that both A and B are heteronuclear diatomic molecules with molecular weights of $m_A = 40$ g/mol, $m_B = 60$ g/mol. The bond lengths are 150 pm and 180 pm and the force constants are 300 N/m and 400 N/m for A and B, respectively. We further assume that the reaction coordinate is along the transitional bond $A\cdots B$ with a vibrational frequency of $\nu_{RC} = 2\times10^{14}$ Hz. (i) What is the order of this reaction? (ii) Calculate the translational, rotational and vibrational contributions to the partition function of A, B and AB. (iii) Calculate the rate constant of this reaction given an activation energy of $\Delta E = 120$ kJ/mol. (1+6+3 pts)

Analytical Chemistry (50%)

Note: You need to present your results using correct significant figures.

7. In a reversed phase chromatography, if five compounds A, B, C, D and E are used in this column. The order of polarity is A > B > C > D > E. Predict the order of the retention time for them to come out from the column. Please express your answer by drawing a figure (spectrum) to show the separation of the mixtures for these five compounds. Please also label the X-axis and Y-axis with proper units for this spectrum. (5%)

8. Define (A) gradient elution (B) isocratic elution used in HPLC. Describe the two methods in details using examples. (C) Which method is better and explain the reason. (9%, each 3%)

9. Mass Spectrometry has become one of the most important and powerful analytical instruments for many fields of study such as biological science, biomedicine, medicine, proteomics, food science, environmental science and biochemical science. Suppose you have the chance to use many different types of mass spectrometers for various purposes, select the following mass instrument(s) to match the proper conditions:
   (A) Select the types of soft ionization techniques which obtained the Award of Nobel Prize in Chemistry in the year of 2002. (1) FI (Field Ionization) (2) MALDI (matrix assisted laser desorption/ionizaiton) (3) ESI (Electrospray Ionization) (4) EI (Electronic Ionization) (5) CI (Chemical Ionization) (6) FD (Field Desorption).(複選)
   (B) Select the most suitable mass spectrometer for quantitative analysis of Hg from sea water? (1) EI-MS (2) CI-MS (3) GC-MS/MS (4) LC-MS/MS (5) ESI-MS (6) ICP-MS (7) MALDI-MS. (單選) (8%, each 4%)

10. You are working on an UV/Visible spectrometer in the experiments of Analytical Chemistry. A 1.52×10^{-4} M solution of potassium permanganate ($KMnO_4$) solution has a transmittance of 39.0% when measured in a 1.0 cm cell at the wavelength of 525 nm. Calculate (A) the absorbance of this solution (B) the molar absorptivity of $KMnO_4$. Please express your results with the proper units also (8%, each 4%)

11. A monochromator (grating type) with a reciprocal linear dispersion of 1.0 nm/mm is used to separate two sodium lines at 588.9950 nm and 589.5924 nm. What slit width would be required for the separation? Use the proper units in your calculations. (8%)

12. You are working on a titration reaction of NaCl solution with $AgNO_3$ solution. Perform calculations needed to generate a titration curve for 50 mL of 0.05 M NaCl with 0.1 M $AgNO_3$ when the $AgNO_3$ solution is added for (A) 10mL (B) 25mL (C) 26 mL (D) Draw the titration curve based on the above results and label the X-axis and Y-axis with proper units for this titration curve. The K_{sp} of AgCl is 1.82×10^{-10}). (8%, each 2%)

13. Select the following instrumental methods which can be applied for melamine (三聚氰胺) analysis from milk ? (1) FT-IR (2) TEM (3) GC-MS/MS (4) LC-MS/MS (5) HPLC (6) ICP-MS (7) GC. (複選) (4%)