題號: 62

國立臺灣大學104學年度碩士班招生考試試題

科目:有機無機

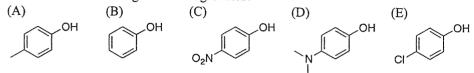
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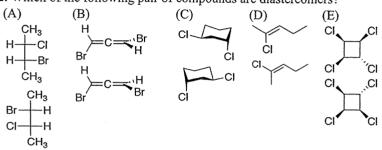
第一部份 有機化學(共50分)

Part I. 單選題(第 1~4 題). Please select the most appropriate answer for the following questions. There is only one correct answer for each question. 請於試卷內之「選擇題作答區」依序作答。(每題 2 分,共 8 分)

1. Which of the following is the strongest acid?



2. Which of the following pair of compounds are diastereomers?



3. Which alkyl halide reacts more rapidly by an S_N1 mechanism?

$$(A) \qquad (B) \qquad (C) \qquad (D) \qquad (E)$$

$$Br \qquad CI \qquad CI \qquad Br$$

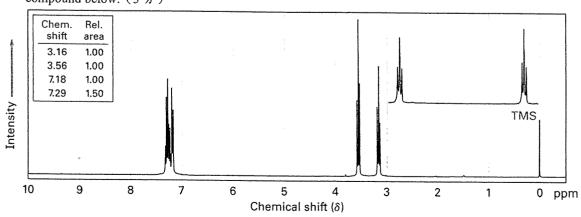
4. Which of the following is the most reactive nucleophile in a polar aprotic solvent?

(A)
$$O^-$$
 (B) O^- (C) O^+ (D) O^- (E) O^+

Part II. 問答題(第 5~7 題). Please provide a short answer for the following questions. 請於試卷內之「非選擇題作答區」依題號順序作答。(共 9 分)

5. Please provide a mechanism for the following transformation. (4分)

6. The ¹H NMR spectra of the compound C₈H₉Br is shown below. Please propose a structure for the compound below. (3 分)



見背面

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7. Please draw the lowest energy chair conformation for the following compound. (2分)

Part III. 簡答題(第 8~20 題). Please draw the major product(s) for the following reactions. Please include stereochemistry when necessary. Line angle structures (also known as skeletal structures) are preferred. 請於試卷內之「非選擇題作答區」依題號順序作答。 (共 33 分)

$$+ 0$$
 $+ 0$
 A
 A

$$H_{+}$$
 H_{-}

$$0 = \bigvee_{NH_3} \bigoplus_{\Delta}$$

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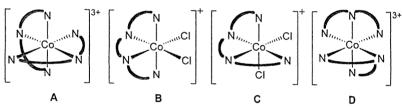
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第二部份無機化學 (共 50 分)

多重選擇題(第 $21 \sim 30$ 題). 每題至少有一個正確選項,每題 5 分,請依題號順序於『選擇題作答區』內作答

- 21. Which of the following statement(s) about fluorine and chlorine is(are) correct?
- a. $Cl_2(g)$ has smaller bond dissociation energy than $F_2(g)$.
- b. NaCl has smaller lattice energy than NaF.
- c. Fluorine is more electronegative.
- d. Fluorine has higher electron affinity.
- e. Fluoride has higher hydration energy.
- 22. Which of the following description(s) of SO₃ is(are) correct?
- a. SO₃ and NH₃ belong to the same point group.
- b. SO₃ is a polar molecule.
- c. SO₃ has three mirror planes.
- d. SO₃ has six degrees of vibrational freedom.
- e. The symmetric stretching vibration of SO₃ is IR inactive.
- 23. Which of the following description(s) is(are) correct?



- a. Compound A belongs to C_{2v} symmetry point group.
- b. The absolute configuration of compound **B** is Λ
- c. The absolute configuration of compound C is Λ
- d. The absolute configuration of compound **D** is $\Lambda\Delta\Delta$
- e. None of the above.
- 24. How to achieve high spin transition metal complexes?
- a. Use π -donating ligands.
- b. Use 3rd row transition metal.
- c. Use metal ions in high oxidation state.
- d. Use metal ions with large paring energy.
- e. Increase the temperature of environment.
- 25. Which of the following description(s) of $[MX_6]^{n}$ ($M = 1^{st}$ row transition metal; X = F, Cl, Br, and I) is(are) correct?
- a. In all cases, the measured Racah parameter B of Mⁿ⁺ is always smaller than that of free metal ion.
- b. Racah parameter B of iodide complex is the smallest in the series due to the poor overlap between p orbital of iodide and d orbital of metal ion.
- c. Crystal field splitting Δ_o of iodide complex is smaller than that of fluoride complex because iodide is less electronegative than fluoride.
- d. One electron oxidation of the complex increases both Racah parameter B and crystal field splitting Δ_{o}
- e. By changing the M from 1st row to 3rd row transition metal ion, Racah parameter B and crystal field splitting Δ_0 of the complex will be increased.

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26. To investigate the ligand substitution mechanism of Co³⁺, a series of aquation and anation reactions were carried out in water. Ligand (L) can be neutral or anionic.

$$\begin{array}{ll} \text{Aquation:} & [L_5 \text{Co} X]^{n^+} + \text{H}_2 \text{O} \ \rightarrow [L_5 \text{Co} (\text{H}_2 \text{O})]^{(n+1)^+} + X^- \\ \text{Anation:} & [L_5 \text{Co} (\text{H}_2 \text{O})]^{(n+1)^+} + Y^- \ \rightarrow [L_5 \text{Co} Y]^{n^+} + \text{H}_2 \text{O} \end{array}$$

If the reaction follows the intimate dissociative mechanism, which of the following phenomenon should be observed?

- a. The anation reaction rate is highly dependent on the nature of Y
- b. The observed transition state volume change is positive
- c. Limiting rate constant for anation is always smaller than the water exchange reaction $(Y = H_2O)$
- d. For a specific X, the aquation reaction rate is not affected by the overall charge of the complex.
- e. The anation rate is first order to [Y] at low concentration of Y.
- 27. If the absorption spectrum of $[Ni(NH_3)_6]^{2+}$ contains three peaks at 9500, 16200, and 27500 cm⁻¹, please select the correct answer(s).
- a. The ground state term of free Ni^{2+} ion is 3F_2
- b. The absorption peak centered at 16200 cm⁻¹ is assigned to transition from ${}^{3}A_{2g}$ to ${}^{3}T_{1g}$
- c. Crystal field splitting of the complex is 11875 cm⁻¹
- d. Racah parameter B of the complexes is 1013 cm⁻¹.
- e. None of the above.
- 28. Which of the following compound(s) features metal-metal bond?

- 29. For metal carbonyl complexes, which of the following statement(s) is(are) correct?
- a. CO is a soft ligand and tends to form stable complexes with high oxidation state metal ions.
- b. The CO stretching frequencies of [Ni(CO)₃L] complexes can be used to quantify the electron donating ability and steric bulkiness of L.
- c. For [Mn(CO)₆]⁺ and [V(CO)₆]⁻, the vanadium complex is more electron rich and has higher CO stretching frequency.
- d. The observed CO stretching frequency in (CO)₅W=C(OMe)Ph is higher than that of W(CO)₆.
- e. None of the above.
- **30.** As shown below, diiron nonacarbonyl (Fe₂(CO)₉) conforms to D_{3h} symmetry with three bridging CO and six terminal CO groups. Please select the correct answer(s).

	D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_{v}$		-
0.0	Aí	1	1	1	1	1	1		$x^2 + y^2, z^2$
	A_2'	1	1	-1	1	1	-1	R_z	
oc co	E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2,xy)
ocFe Feco	A_1''	1	1	1	-1	-1	-1		
	A_2''	1	1	-1	-1	-1	1	z	
00 0 00	E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)
					,				

- a. The symmetries of d orbitals in D_{3h} point group are $A_1 + E' + E''$
- b. The stretching vibration symmetries of the three bridging CO groups are $A_1'' + E'$
- c. The stretching vibration symmetries of the six terminal CO groups are $A_1' + A_2'' + 2E'$
- d. There are totally three IR active CO stretching vibrations.
- e. None of the above.