題號: 67

國立臺灣大學101學年度碩士班招生考試試題

科目:有機無機

節次: 6

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共 4 頁之第 1 頁

第一部分 有機化學 (共50分)

第1~12題:多重選擇題

(每題至少有一正確選項,每題3分,請依題號順序於『選擇題作答區』內作答)

1. For the reaction scheme shown below, which is (are) correct structure(s) for I-II?

2. Which is the major product from the reaction shown below?

- 3. Which one of the following alkyl halides would be expected to give the <u>highest</u> ratio of elimination to substitution on treatment with sodium ethoxide in ethanol?
 - (A) 2-bromopentane (B) 3-bromopentane (C) 1-bromo-2-methylbutane (D) 2-bromo-2-methylpentane
 - (E) 1-bromo-3-methylbutane
- 4. Which of the resulting product from the following reactions is (are) in a pair of enantiomers?

5. Which reagent is (are) suitable for the following transformation?

6. Which of the following sequences of acidity for compounds A~E is arranged in the correct order?

- (A) B > D > C > A > E (B) B > C > D > A > E (C) B > C > D > E > A (D) C > B > D > A > E
- (E) C > D > B > E > A
- 7. Which of the following reagents does undergo conjugated addition (1,4-addition) to 2-cyclohexenone?
 - (A) $CH_3CH_2NH_2$ /ethanol (B) $(CH_3)_3N/CH_3OH$ (C) LiAlH₄; followed by H_3O^+
 - (D) Ph_2CuLi /ether; followed by H_3O^+ (E) $CH_2(COOCH_3)$ /NaOCH $_3$; followed by H_3O^+

見背面

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8. Which is (are) the product(s) from the acid-catalyzed dehydration of III?

$$\bigcirc \mathsf{H} \longrightarrow ? (\mathsf{A}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{B}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{C}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{B}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{C}) \longrightarrow (\mathsf{C}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{C}) \longrightarrow (\mathsf{C}) \bigcirc \mathsf{H} \longrightarrow (\mathsf{C}) \longrightarrow (\mathsf{$$

9. Which of the following molecules would be expected to show aromatic character?

$$(A) \quad \bigcirc P\text{-}CH_3 \quad (B) \quad \bigcirc P\text{-}CH_3 \quad (C) \quad \bigcirc N \quad (D) \quad \bigcirc N \quad (E) \quad (E) \quad \bigcirc N \quad (E) \quad$$

- 10. Which of the following indicated –**H** would be <u>completely</u> deprotonated by the treatment of equal molar amount of NaNH₂?
 - (A) **H**-CH(C≡N)₂
- (B) CH₃CH₂OCH₂-H
- (C) C₆H₅C≡C-H (D) (CH₃)₂CHO-H

- (E) $(CH_3)_2C=CH-H$
- 11. Which of the following reactions will proceed via a S_N2 pathway?

12. Which of the following is (2R,3S)-2,3-dibromopentane?

$$(A) \begin{array}{c} H \\ Br \\ CH_2CH_3 \\ H \\ CH_2CH_3 \\ \end{array} \\ (B) \begin{array}{c} H \\ Br \\ H \\ \end{array} \\ (C) \begin{array}{c} Br \\ Br \\ H \\ \end{array} \\ (D) \begin{array}{c} Br \\ Et \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ Br \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array} \\ (E) \begin{array}{c} CH_2CH_3 \\ H \\ CH_3 \\ \end{array}$$

第13~15題問答題,請於試卷內之「非選擇題作答區」標明題號依序作答。

13. (4 分) The spectral data of compound A are shown as following:

ESI-MS: m/z for molecular ion M^+ = 86.07.

IR: 3400 cm⁻¹, 1638 cm⁻¹.

¹H NMR δ 5.71 (triplet, J = 7 Hz, 1H), 4.12 (doublet, J = 7 Hz, 2H), 3.80 (broad singlet, 1H), 1.72 (singlet, 3H), 1.60 (singlet, 3H).

¹³C NMR δ 135.1, 124.0, 59.2, 26.2, 18.3.

Please provide the correct structure of A. Rationalize your answer.

14. (5 分) Provide a reasonable mechanism for each of the following reactions.

$$(A)$$
 HO
 OH
 (B)
 OH
 HBr
 Br

15. (5 分) Provide two different synthetic approaches for the following transformation.

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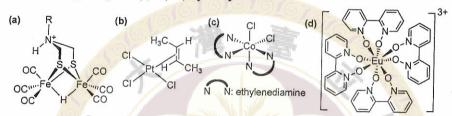
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第二部份 無機化學(共50分)

第 16 ~19 題:多重選擇題,每題4分,請依題號順序於『選擇題作答區』內作答

- 16. Which of the following statement(s) is(are) correct?
 - a. Solubility in water: NaF > NaCl > NaBr > NaI
 - b. The Hammett acidity function of a HF-BF3 system is lower than that of pure HF.
 - c. Lithium is a stronger reducing agent than potassium in aqueous solution.
 - d. Thiocyanate (SCN) bonds to Hg²⁺ though nitrogen, but attaches to Zn²⁺ with sulfur.
- 17. Which of the following compound(s) is(are) optically active?

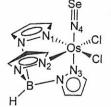


- 18. Which of the following compound(s) has(have) magnetic moment very close to 2.83?
 - (a) $[Cr(H_2O)_6]^{2+}$

 - (b) [V(H₂O)₆]³ (c) [Ni(CN)₄]²
 - (d) $[Mn(CN)_6]^3$
- 19. Which of the following compound(s) features metal-metal multiple bonds?
 - (a) Re₂Cl₄(OAc)₂
 - (b) Cu₂(OAc)₄
 - (c) Rh₂(OAc)₄
 - (d) Mo₂(OAc)₄

第 20 ~ 25 題問答題,請<mark>於試卷</mark>內之「非選擇題作答區」標明題號依序作答

20. (4分) Selected structural information of an osmium complex is listed below. Please briefly explain why the Os-N₃ bond is longer than Os-N₁ and Os-N₂ bonds? Why is the NSe stretch (v_{NSe}) of the complex at higher frequency than that of free NSe gas molecule? (Hint: the N-O bond distance in [NO][PF6] is shorter than that of NO molecule.)



Os-N₁: 2.066(8) Å

Os-N2: 2.069(7) Å

Os-N3: 2.101(7) Å

v_{N∈Se}: 1156 cm⁻¹ (NSe gas: 945 cm⁻¹) 題號: 67 國立臺灣大學101學年度碩士班招生考試試題

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21. (4分) Please assign the point group for the following compounds:

22. (6分) Consider the following nitro-nitrito isomerization reaction. One isomer is yellow, and the other is red. Which isomer is more stable? What is the identity of the yellow isomer? Explain briefly.

23. (6分) Please complete a catalytic cycle for the following hydrogenation reaction catalyzed by the Wilkinson's catalyst, RhCl(PPh₃)₃. For each species in the catalytic cycle, formal oxidation state of Rh and electron counts of the complexes must be included.

- 24. (6分) The d² ions CrO₄⁴, MnO₄³, and FeO₄² have intense charge-transfer transitions. Please order these ions according to their CT transition wavelength, Δ_t, and oxidation power. Explain briefly.
- 25. (8分) Construct a molecular orbital energy level diagram of PCl₅ with symmetry-adapted linear combination of orbitals. What types of hybrids can be used in bonding to axial and equatorial chlorine atoms? Which P-Cl bond (axial or equatorial) is longer? Explain briefly.

D_{3h} $(\overline{6})_{m2}$	Ε	2C ₃	3C ₂	σ_h	2S ₃	3σ,	il s		
A' ₁	1	1	I	1	1	1		$x^2 + y^2, z^2$	
A_2^{\prime}	1	1	-1	1	1	-1	R_z		
E'	2	-1	0	2	-1	0	(x, y)	$(x^2-y^2,2xy)$	
A"	1	1	1	-1	-1	-1			
A_2''	1	1	-1	-1	-1	1	z		
E"	2	-1	0	-2	1	0	(R_x, R_y)	(xy, yz)	

試題隨卷繳回