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國立臺灣大學 107 學年度碩士班招生考試試題

C¹³ NMR: δ 69.20 145.15 127.80, 128.39 128.78

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有機部份 (50分)

(b)

第一題 寫出下列化合物 IUPAC 名稱。(各 2 分, 共 8 分)

Problem 1 Give IUPAC name for the following compounds. (8 pts)

$$A$$
 B
 C
 NO_2
 OI
 OI
 OI
 OI

第二題 寫出下列化合物結構式。(共24分)

Problem 2 Predict the products of the following reactions. (24 pts)

Si— O H BH₃ Compound G (化合物 G 2 分)

CuCN Compound O (化合物 O 2 分)

(i) CH₂I₂ Compound R (化合物 R 2 分)

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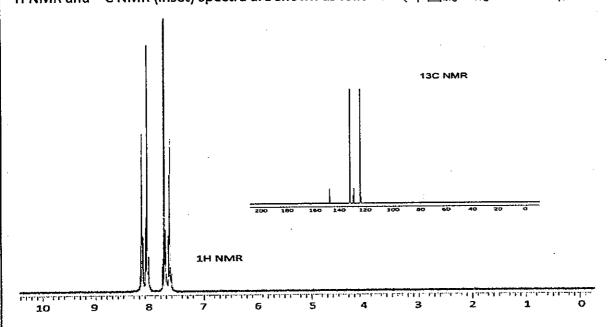
第三題 (共8分)

Problem 3 (8 pts)

(a) 寫出化合物 S 結構式。 (2 分). What is the structural formula of S? (2 pts)

Molecular weight of S(S的分子量): 202.005;

 1 H NMR and 13 C NMR (inset) spectra are shown as follows (下圖為 S 的 1 H NMR 和 13 C NMR (插圖))



(b) 寫出化合物 T, U, V 結構式。(各 2 分) Predict the chemical structures of T (2 pts), U (2 pts), and V (2 pts).

化合物 V 分子式 為 C10 H12O4,其 NMR 與 IR 光譜如下:

Compound V, with a molecular formula of C₁₀ H₁₂O₄, shows the following spectral data

 1 H NMR (400 MHz, CDCl₃) δ 5.71 (s, 2H), 3.78 (s, 6H), 3.0 (s, 4H);

 13 C NMR (100 MHz, CDCl₃) δ 168.5, 132.5, 122.4, 52.2, 27.5;

IR (cm⁻¹) 3038, 2998, 2952, 2884, 2843, 2827, 1724, 1681, 1644, 1434, 1256, 1063.

第四題 環己烯,1,3-環己二烯,與苯的氫化熱分別為 28.6 kcal/mol, 55.4 kcal/與 49.8 kcal/mol。按上述數據,估算苯的芳香 穩定共振能,並提出說明。 (2 分)

Problem 4 The heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene are 28.6 kcal/mol, 55.4 kcal/mol, and 49.8 kcal/mol respectively. On the basis of these data, estimate the aromatic stabilization energy (the resonance energy) of benzene. Give explanations to support your estimation. (2 pts)

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第五題 寫出下列反應之機構。 (3分)

Problem 5 Propose reaction mechanisms for the following transformation. (3 pts)

$$\begin{array}{c|c} CH_3 & O \\ O & O \\ O & CH_3 \end{array} \xrightarrow{\tilde{E}} CH_3 \end{array} \xrightarrow{t\text{-BuOK}} \begin{array}{c} O \\ O \\ O \\ \end{array}$$

第六題 提出下圖的合成策略,試劑庫中的試劑,或其他少於三碳(含)有機試劑均可使用。 (5分)

Problem 6 How could you carry out the following transformation? Either the reagents listed in the following reagent tool box or reagents less than 3 carbons can be used. (5 pts)

Reagent tool box (試	劉庫)			
N-Br	СІ ОООН	n N		
KHSO ₄	OH OH	H ₂ O ₂		
CHCl₃		-\sigma_o\ci	H-C≌C-H	
Fe	Ni	NH ₃	NaNH ₂	
Li	Na	Mg	K	
NaBH4	BH ₃	PBr ₃	Br ₂	
SOCl ₂	HCI	Pd/C, H₂	F	
<u>}</u> -0-κ⁺	NaOH	CH₃−O⁻K⁺	OsO ₄	
HgSO ₄	CH ₂ I ₂ , Zn/Cu	NalO ₄	O ₃ / Ma ₂ S	

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無機部份 (共50分)

第1~5題:多重選擇題,每題4分(錯一個選項2分,錯兩個選項0分),請依題號順序於『選擇題作答區』內作答。

- 1. Which of the following description of metallic and ionic solid is/are correct?
 - a. The packing density of simple cubic is lower than that of diamond structure.
 - b. In an interstitial alloy, the atomic radii difference between guest element and host element should be less than 15%.
 - c. The calculated lattice enthalpy of LiF using Born-Mayer equation is expected to differ substantially from the experimental value obtained from Born-Haber cycle.
 - d. The non-stoichiometric Fe₂O_{3-x} oxide is an n-type semiconductor.
 - e. None of the above.
- 2. Which of the following description of acids is/are correct?
 - a. HNO₃ and HSO₃F behave as bases in liquid H₂SO₄.
 - b. $HClO_4$ (p $K_a = -10$) is more acidic than HCl (p $K_a = -8$) in water.
 - c. Acetic acid $(pK_{ion} = 14.5)$ is a better solvent than water $(pK_{ion} = 14)$ in determining the acidity difference of acids.
 - d. The pH value of water at higher temperature is smaller.
 - e. None of the above.
- 3. Which of the following description of chemical bonds is/are correct?
 - a. M-M π -bond for heavier metal is always weaker than that of the lighter metals in the same group.
 - b. C-O single bond is stronger than Si-O single bond due to the better overlap between 2p orbitals.
 - c. The M-C bond in [V(CO)₆] is stronger than that in [Mn(CO)₆]⁺.
 - d. There is M-M single bond in Re₂(CO)₁₀ and Fe₂(CO)₉.
 - e. None of the above.
- 4. Which of the following description of a [NiL₆]²⁺ complex is/are correct?
 - a. The ground state term of the complex is ${}^3T_{Ig}$
 - b. The Δ_0 can be estimated from the lowest d-d transition band.
 - c. The absorption bands of $[Ni(H_2O)_6]^{2+}$ are lower in energy compared to that of $[Ni(en)_3]^{2+}$.
 - d. If the central metal ion is replaced by Pt²⁺, all absorption bands will be red-shifted.
 - e. None of the above.
- 5. Which of the following description of organometallic complexes is/are correct?
 - a. The associative ligand substitution of [NiL₄] ($L = P(OEt)_3$) can be promoted by changing the L from $P(OEt)_3$ to $P(O^iPr)_3$.
 - b. A cis orientation of eliminating ligand is required for concerted reductive elimination.
 - c. Reductive elimination of ligands can be promoted by oxidation of the metal center.
 - d. For an 18-electron L_n M-Bn complex (Bn = benzyl), dissociation of a *cis*-ligand is required for β -hydride elimination.
 - e. None of the above.

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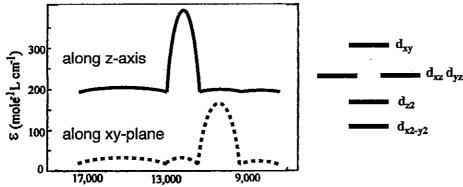
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第 6~8 題問答題,請依題號順序於『非選擇題作答區』內作答,並應註明作答之部份及題號。

6. Please give the dⁿ configuration of the central metal ion and the total electron count of the metal complex. (12 points)

a.
tBu
 b. PR_2 c. NC PMe_3 tBu tBu

- 7. Please answer the following questions about a $C_4B_2H_6$ molecule:
 - a. Classify the compound according to Wade's rule. Justify your answer (4 points)
 - b. Structure of all isomers and their corresponding symmetry point group. (6 points)
- 8. It is known that a tetra-coordinate Cu²⁺ complex adopts D_{2d} geometry in solid state. With the given d-orbital splitting, please assign the transition bands (12,000 cm⁻¹ and 10,000 cm⁻¹) shown in the polarized absorption spectrum. (8 points)



$\frac{D_{2d} = V_d}{\left(\overline{42}\right)m}$	E	254	C ₂	2C' ₂	2σ _d		
Aı	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
$\mathbf{B_{I}}$	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1	z	ху
E	2	0	- 2	0	0	(x, y) (R_x, R_y)	(xz, yz)

試題隨卷繳回