

國立中正大學

114 學年度碩士班招生考試

試題

[第 4 節]

科目名稱	有機無機化學
系所組別	化學暨生物化學系

—作答注意事項—

※作答前請先核對「試題」、「試卷」與「准考證」之系所組別、科目名稱是否相符。

1. 預備鈴響時即可入場，但至考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。
2. 考試開始鈴響時，即可開始作答；考試結束鈴響畢，應即停止作答。
3. 入場後於考試開始 40 分鐘內不得離場。
4. 全部答題均須在試卷（答案卷）作答區內完成。
5. 試卷作答限用藍色或黑色筆（含鉛筆）書寫。
6. 試題須隨試卷繳還。

國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

本科目共 6 頁 第 1 頁

系所組別：化學暨生物化學系

科目：無機化學，總分 50 分

1. Please assign the point groups.

a. XeF_4 _____ b. $\text{O}=\text{S}(\text{CH}_3)_2$ _____ c. $\text{O}=\text{C}(\text{CH}_3)_2$ _____ d. ClF_3 _____. (4 points)

2. Determine the number of IR-active C-O stretching vibrations for (a) *fac*- $\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$ and (b) *mer*- $\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$. (6 points)

3. Analysis of H_2O gives the Lewis structure and reducible representation (Γ):

(a) Classify the irreducible representations into translational, rotational, and vibrational modes.

(b) Which vibrational modes are Infrared and Raman active? (6 points)

4. Determine the hybrid-orbital type of the central atoms in SF_4 and $[\text{Ni}(\text{CN})_4]^{2-}$. (6 points)

5. Provide explanations for the following:

(a) The boiling points of the noble gases increase with atomic number.

(b) Methanol (CH_3OH) has a much higher boiling point than methyl mercaptan (CH_3SH).

(c) PCl_5 is a stable molecule, but NCl_5 is not. (6 points)

6. Calculate the electron affinity of Cl from the following data for NaCl : Cl_2 bond energy = 239 kJ/mol; $\Delta H_f(\text{NaCl}) = -413$ kJ/mol; $\Delta H_{\text{sub}}(\text{Na}) = 109$ kJ/mol; $\text{IE}(\text{Na}) = 496$ kJ/mol; $U = -789$ kJ/mol. (4 points)

7. Determine the number of unpaired electrons for the following complexes:

(a) $[\text{Co}(\text{CO})_4]$, (b) $[\text{Co}(\text{CN})_6]^{4-}$, (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$. (4 points)

8. Exchange of an H_2O ligand on $[(\text{CO})_3\text{Mn}(\text{H}_2\text{O})_3]^+$ is much more rapid than on the analogous $[(\text{CO})_3\text{Re}(\text{H}_2\text{O})_3]^+$. The activation volume (change in volume on formation of the activated complex) is $-4.5 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$. The Mn complex has infrared bands at 2051 and 1944 cm^{-1} that can be attributed to C-O stretching vibrations.

(a) Suggest why the Mn complex reacts more rapidly than the analogous Re complex.

(b) Is the activation volume more consistent with an A (or I_a) or a D (or I_d) mechanism? Explain. (4 points)

9. Predict the products of the following reactions:

(a) $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2 + h\nu \rightarrow ?$

(b) $[\text{Mn}(\text{CO})_5]^- + (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br} + \text{heat} \rightarrow ?$

(c) $[\text{Mn}(\text{CO})_5]^- + \text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{Cl} \rightarrow -\text{CO} \rightarrow ?$ (6 points)

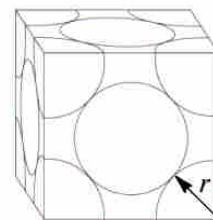
國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

本科目共 6 頁 第 2 頁

系所組別：化學暨生物化學系

10. What percent of the total volume is occupied by spheres in (a) a face-centered cube (see figure on right) and (b) a body-centered cube in which all atoms are identical. (4 points)



D_{nh} GROUPS

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1	R_z	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_y	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_x	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1		yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$		
A_1'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	(x, y)	$(x^2 - y^2, xy)$
E'	2	-1	0	2	-1	0		
A_1''	1	1	1	-1	-1	-1	z	
A_2''	1	1	-1	-1	-1	1	(R_x, R_y)	(xz, yz)
E''	2	-1	0	-2	1	0		

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		(xz, yz)
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

C_{nv} GROUPS

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

本科目共 6 頁 第 3 頁

系所組別：化學暨生物化學系

科目：有機化學，總分 50 分

1. Draw the structures of the following compounds. (1 pt each, 6 pts)

(1) *m*-xylene

(2) imidazole

(3) *p*-benzoquinone

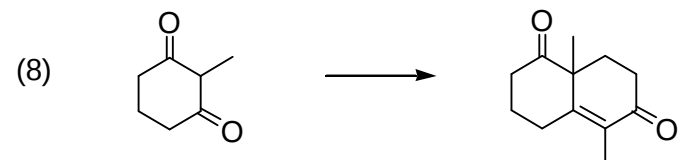
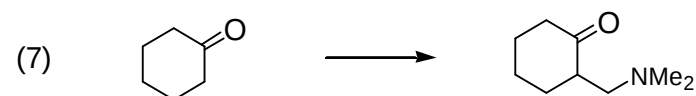
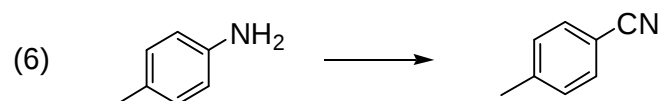
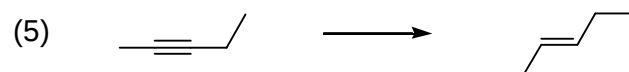
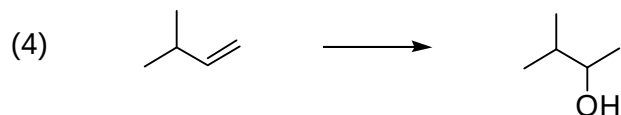
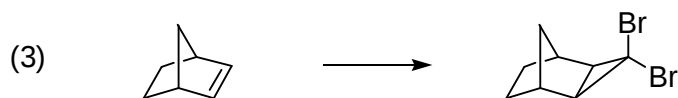
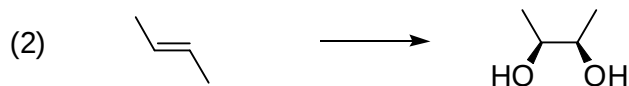
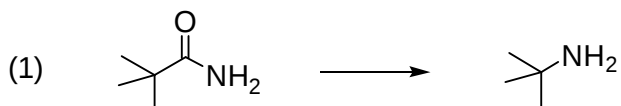
(4) quinoline

(5) phenanthrene

(6) thiophene

2. Suggest a reagents (or a series of reagents) that can be used to accomplish the following transformation.

(2 pts each, 16 pts)



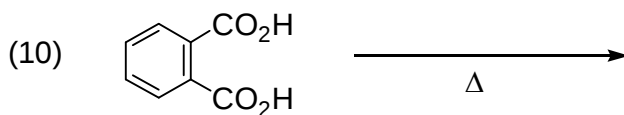
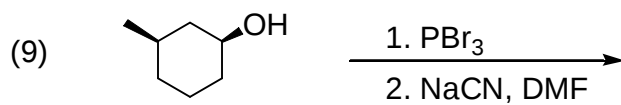
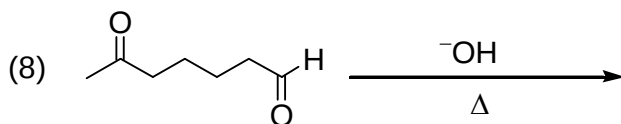
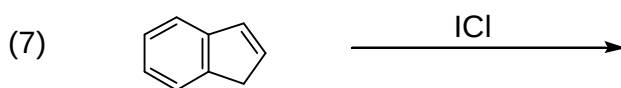
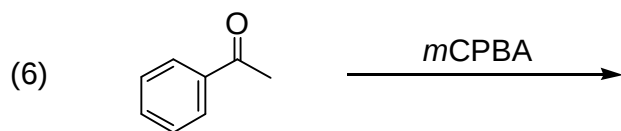
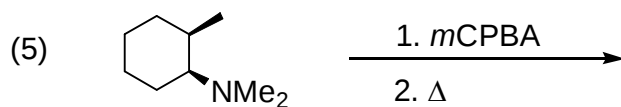
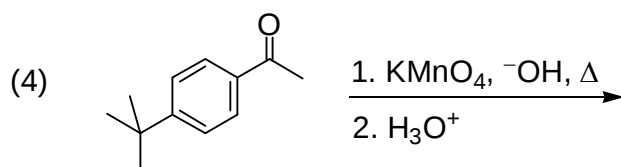
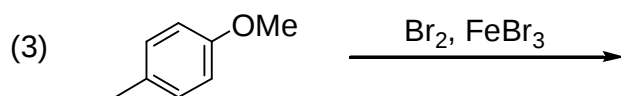
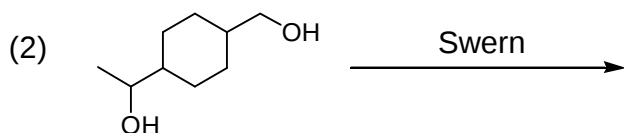
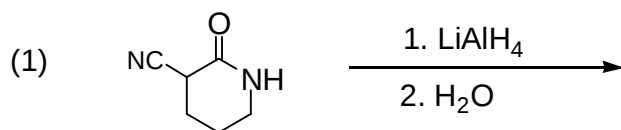
國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

本科目共 6 頁 第 4 頁

系所組別：化學暨生物化學系

3. Give the expected major product with appropriate stereochemistry, if necessary. (2 pts each, 20 pts)



國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

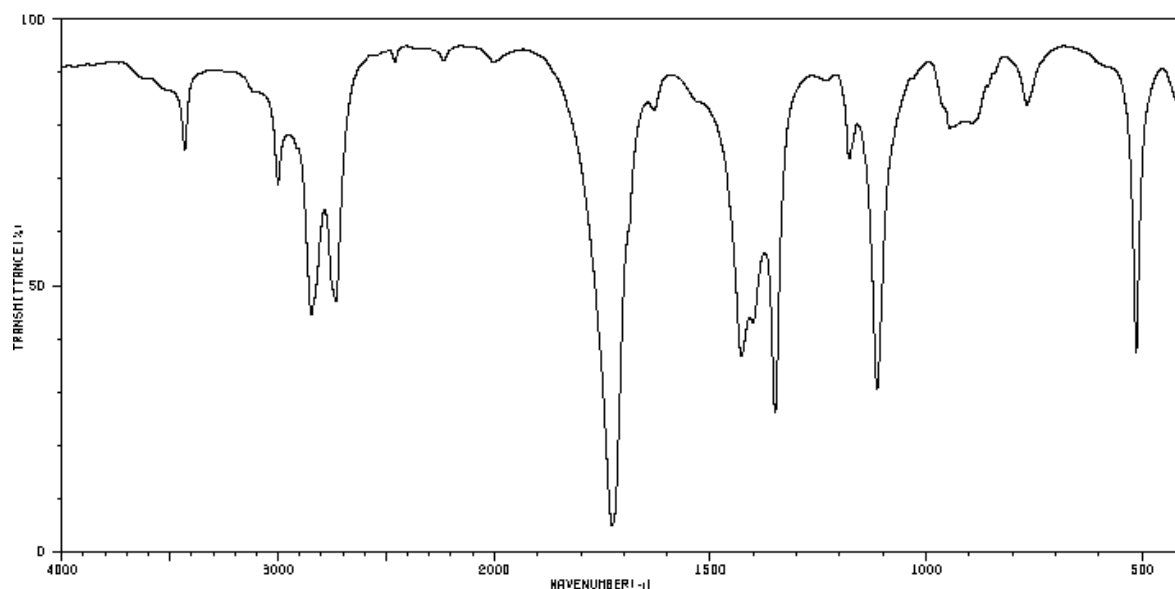
本科目共 6 頁 第 5 頁

系所組別：化學暨生物化學系

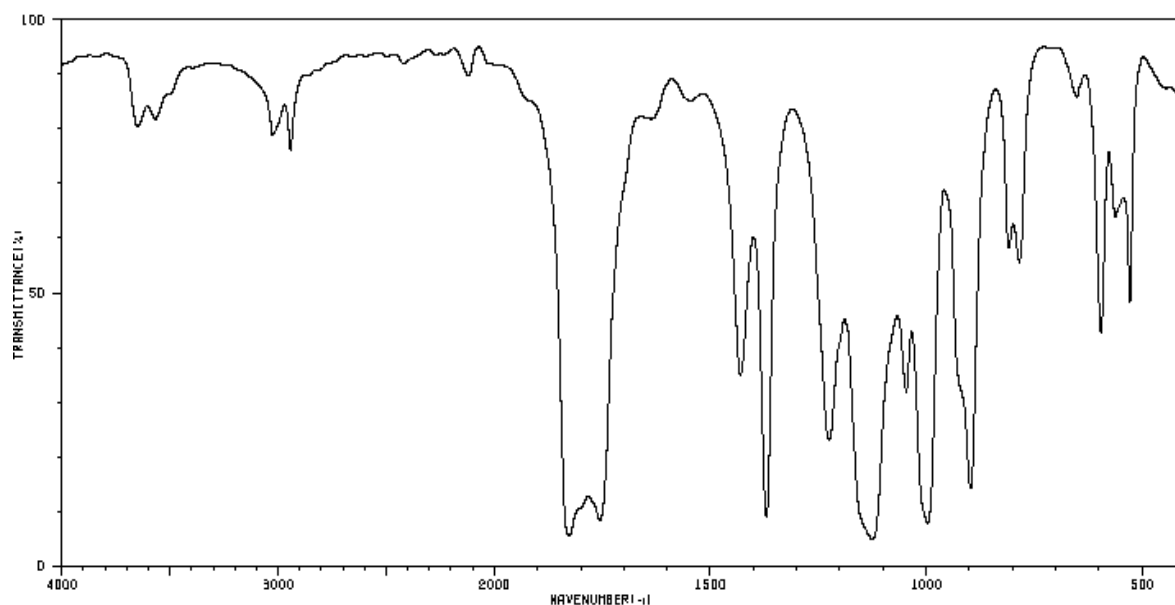
4. Match the compound to the following IR spectrum. (2 pts each, 8 pts)



(1)



(2)



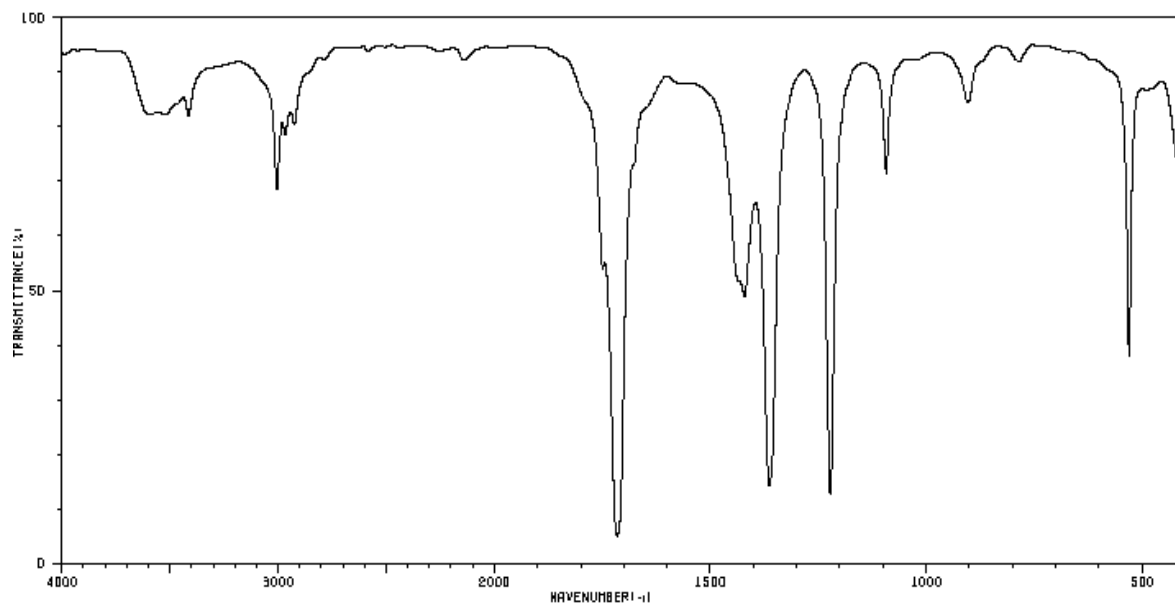
國立中正大學 114 學年度碩士班招生考試試題

科目名稱：有機無機化學

本科目共 6 頁 第 6 頁

系所組別：化學暨生物化學系

(3)



(4)

