國立中正大學
109 學年度碩士班招生考試
試 題

[第 3 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。

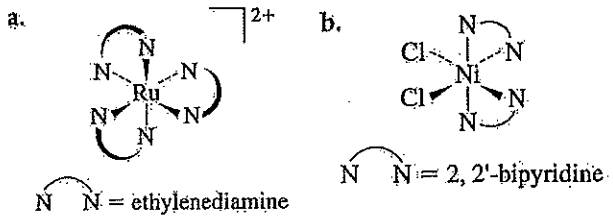
1. 預備鈴響時即可入場，但至考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。
2. 考試開始鈴響時，即可開始作答；考試結束鈴響畢，應即停止作答。
3. 入場後於考試開始 40 分鐘內不得離場。
4. 全部答題均須在試卷（答案卷）作答區內完成。
5. 試卷作答限用藍色或黑色筆（含鉛筆）書寫。
6. 試題須隨試卷繳還。

1. Please assign the point groups.
(a) B_3H_8 ___, (b) cyclohexane: chair form ___; boat form ___, (c) **96** ___. (4 points)

2. Determine the hybrid-orbital types of the central atoms in ClF_3, BF_3, and PF_5. (6 points)

3. Some of the products of the following reactions are insoluble, and some form soluble adducts. Consider only the HSAB characteristics in your answers.
(a) Will Cu^{2+} react more strongly with OH^- or NH_3? With O^{2-} or S^{2-}?
(b) Will Fe^{3+} react more strongly with OH^- or NH_3? With O^{2-} or S^{2-}?
(c) Will Ag^+ react more strongly with NH_3 or PH_3? Will Fe, Fe^{2+}, or Fe^{3+} react more strongly with CO? (6 points)

4. Assign absolute configurations (Λ or Δ) to the following: (4 points)



5. Given rational accounts for the following observations:
(a) The formation constant for the addition of a third molecule of en to Cu^{2+} is much lower than for Ni^{2+}.
(b) Tetrahedral complexes are much more common for Co^{2+} than for Ni^{2+}.
(c) Ligands such as CO and phosphines tend to stabilize the low oxidation states of the transition metals. (en=ethylenediamine) (6 points)

6. (a) Explain the effect on the d-orbital energies when an octahedral complex is compressed along the z axis. (b) Explain the effect on the d-orbital energies when an octahedral complex is stretched along the z axis. In the limit, this results in a square-planar complex. (4 points)

7. (a) The CO exchange reaction $Cr(^{12}CO)_6 + {}^{13}CO \rightarrow Cr(^{12}CO)_5(^{13}CO) + {}^{12}CO$ has a rate that is first order in the concentration of $Cr(^{12}CO)_6$ but independent of the concentration of ^{13}CO. What does this imply about the mechanism of this reaction?
(b) The reaction $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ [R = P(*n*-C_4H_9)$_3$] has the rate law of rate = $k_1[Cr(CO)_6] + k_2[Cr(CO)_6][PR_3]$. Why does this rate law have two terms? (4 points)

8. Determine the ground terms for high- and low-spin d^6 configurations in an O_h symmetry. (4 points)

9. Determine the unknown quantity: (6 points)

(a) $Br(CO)_xRe{=}C(OCH_3)_2$,

(b) $[Ni(NO)_3(SiMe_3)]^x$ (contains linear M-N-O),

(c) $[(\eta^5\text{-}C_5H_5)Mn(CO)_y]_2$ (has a Mn=Mn double bond).

10. Predict the number of infrared-active C-O stretching vibrations for $W(CO)_3L_3$ assuming in a *fac* or *mer* geometry. (6 points)

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_{nh} GROUPS

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		
A'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
E'	1	ε	ε^*	1	ε	ε^*	(x, y)	$(x^2 - y^2, xy)$
	1	ε^*	ε	1	ε^*	ε		
A''	1	1	1	−1	−1	−1	z	
E''	1	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*$	(R_x, R_y)	(xz, yz)
	1	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon$		

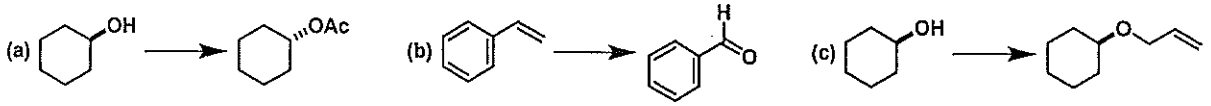
$\varepsilon = e^{(2\pi i)/3}$

D_{nh} GROUPS

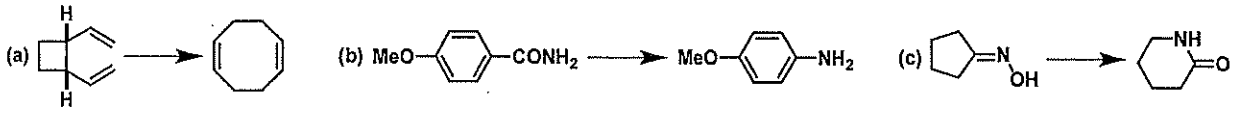
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	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)	(xz, yz)

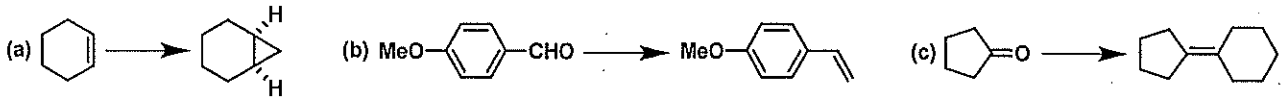
11. (1 point) Which of the following transformations can be carried out by the Mitsunobu reaction?



12. (1 point) Which of the following transformations can be carried out by the Beckmann rearrangement?

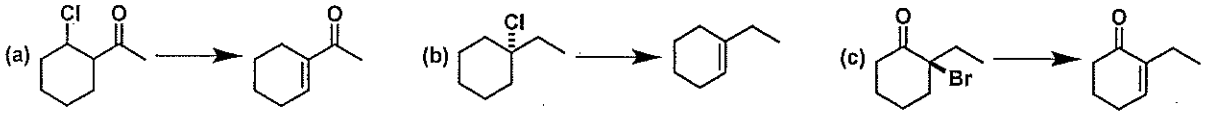


13. (1 point) Which of the following transformations can be carried out by the Wittig reaction?

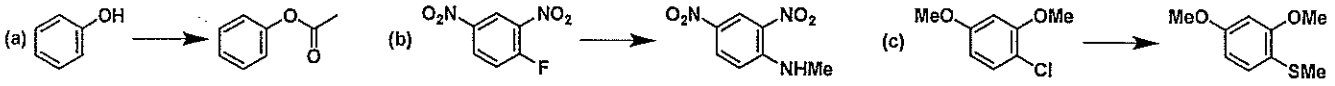


14. (1 point) Which of the following transformations is the best result of a S_N2 reaction?

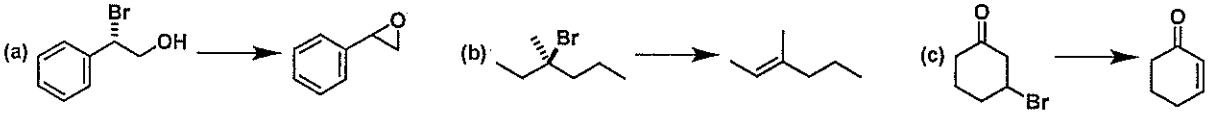
15. (1 point) Which of the following transformations is the result from an E1cb reaction?



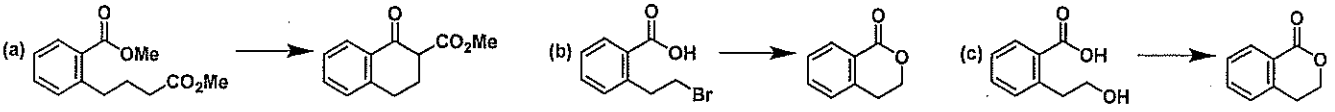
16. (1 point) Which of the following transformations is the result from a S_NAr reaction?



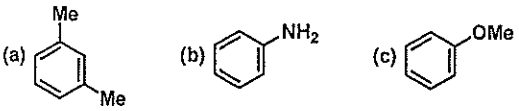
17. (1 point) Which of the following transformations is the result from an E2 reaction?



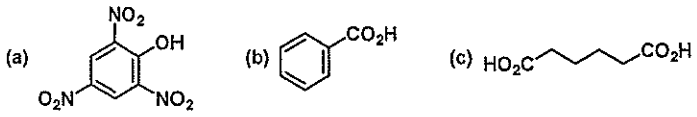
18. (1 point) Which of the following transformations can be carried out by the Dieckmann reaction?



19. (1 point) Which of the following compound is anisole?

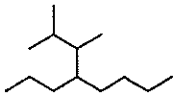


20. (1 point) Which of the following compound is picric acid?

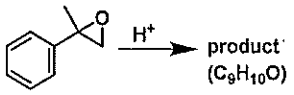


21. (3 points) Give structure each of the following names: (a) indole and (b) cumene.

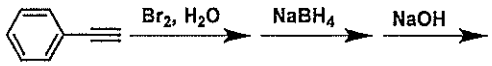
22. (3 points) What is the IUPAC name for the below compound?



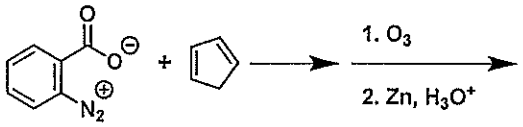
23. (3 points) Give the product of the below reaction transformation:



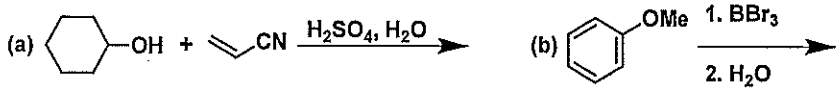
24. (3 points) Give the final product of the below synthesis:



25. (3 points) Give the final product of the below synthesis:



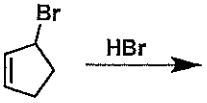
26. (3 points) Predict the product for each reaction below:



27. (3 points) Propose a structure for the compound that fits the following proton NMR spectral data: C_9H_{12}; δ 6.18 (t, 2H), 2.90 (t, 2H), 2.80 (t, 4H), 1.50 (t, 4H)

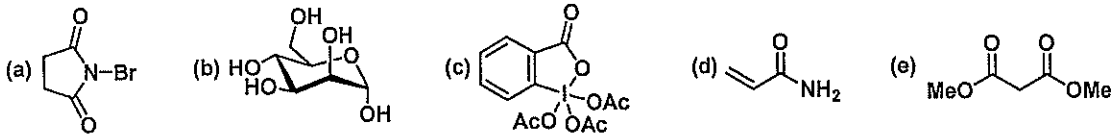
28. (3 points) Give structures of the intermediate and the product of the below synthetic scheme:

29. (3 points) Give the product of the following reaction. Make sure to indicate the stereochemistry, if applicable.



30. (3 points) Using reaction scheme to show all products from glycine reaction with ninhydrin.

31. (5 points) What are common names of the following compounds:



32. (5 points) Starting from benzene, how would you synthesize the following aromatic compound? Assume that *ortho* and *para* isomers can be chromatographically separated.