# 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<u>系所組別、科目名稱</u>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、書記、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。



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系所組別:化學暨生物化學系

#### 科目: 有機化學,總分50分

1. Provide the missing reagents and structural formulas for the major organic products (A-T) from each of the following syntheses. More than one reaction may be necessary in some cases. (2 pts each, 40 pts)

(1) 
$$\frac{OH}{K_2CO_3}$$
 A  $\frac{Li}{NH_3, EtOH}$  B  $\frac{C}{C}$ 

(2) 
$$\begin{array}{c|c} \hline 1. \ Br_2, \ FeBr_3 \\ \hline 2. \ OH^-, \ H_2O \end{array} \qquad D \qquad \begin{array}{c|c} \hline E \\ \hline N_2^+ \\ \hline \end{array} \qquad \begin{array}{c|c} F \\ \hline Br \\ \hline \end{array} \qquad \begin{array}{c|c} F \\ \hline Br \\ \hline \end{array}$$

(3) 
$$PCI_5$$
  $G$   $NaNH_2$   $H$   $I$   $Br_2$   $Br$   $Br$ 

(4) 
$$H^+ \longrightarrow K \xrightarrow{\text{peroxide, } \Delta} L \xrightarrow{\text{$t$-BuOK}} M$$

(5) OH 
$$\stackrel{\text{N}}{\longrightarrow}$$
 CHO  $\frac{1. \text{ Me}_2\text{NH}}{2. \text{ NaBH}_3\text{CN}}$  O  $\frac{1. \text{ H}_2\text{O}_2}{2. \Delta}$  P

(6) 
$$CO_2Me$$
  $R$   $OHC_1$   $CHO$   $CO_2Me$   $MeO_2\tilde{C}$ 

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- 2. Which reagent in each pair listed here would be the more reactive nucleophile in the indicate solvent. (1 pt each, 3 pts)
  - (1)  $F^-$  or  $\Gamma^-$  (in MeOH)
  - (2)  $Cl^-$  or  $Br^-$  (in DMF)
  - (3)  $HO^-$  or  $CH_3CO_2^-$  (in HMPA)
- 3. How many chiral centers are there in the following compounds? (1 pt each, 4 pts)

4. What is the structure of the compound in the following <sup>1</sup>H NMR spectral data with the molecular formula C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>? (3 pts)

 $^{1}\text{H}$  NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.69 (s, 8H).

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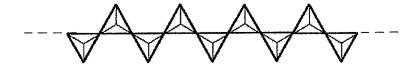
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系所組別:化學暨生物化學系

#### 科目:無機化學

共 19 題,1-13 題每題 2 分,14 及 15 題每題 3 分,16 及 17 題每題 4 分,18 及 19 題每題 5 分,合計 50 分。

- 1. What are the values of quantum numbers n and l for a 5d electron?
- 2. Which one of the following atoms, Na, Mg, Al, has the highest ionization energy?
- 3. Which one of the molecules, OCl<sub>2</sub>, O(CH<sub>3</sub>)<sub>2</sub>, and O(SiH<sub>3</sub>)<sub>2</sub> has the largest bond angle at the O atom?
- 4. For NO, NO, NO, (A) which one has the weakest bond, (B) which one has the most unpaired electrons, on the basis of molecular orbitals?
- 5. List the following acids in order of their acid strength when reacting with NH<sub>3</sub>: BMe<sub>3</sub>, B(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>3</sub>, BF<sub>3</sub>
- 6. Using appropriate chemical equation explain that the conductivity of BrF<sub>3</sub> is increased by adding KF.
- 7. Give an example of p-type semiconductor?
- 8. Determine the formula of the silicate shown below.



- 9. List all the possible first-row transition metals which form complexes [MCl<sub>6</sub>]<sup>4-</sup> having two unpaired Electrons.
- 10. Which one of the following ions,  $CrO_4^{4-}$ ,  $MnO_4^{3-}$ ,  $FeO_4^{2-}$ , has the largest value of  $\Delta_t$ ?
- 11. Predict the product of the mixing equimolar [Pt(CO)Cl<sub>3</sub>] and NH<sub>3</sub>.
- 12. On the basis of the 18-electron rule, determine the second-row transition metal for [M(PE<sub>3</sub>)<sub>2</sub>(NO)<sub>2</sub>]<sup>+</sup> (contains linear M—N—O).
- 13. The tungsten alkylidyne complex W(≡CCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>3</sub> has been used to catalyze the ring-closing metathesis reaction for alkynes. Predict the structure of the cyclic product for metathesis of MeC≡C(CH<sub>2</sub>)<sub>8</sub>COO(CH<sub>2</sub>)<sub>9</sub>C≡CMe.
- 14. (A) Give the Lewis structure, (B) predict the geometry on the basis of VSEPR and (C) determine the point group of TeF<sub>4</sub><sup>2</sup>.
- 15. Sketch all the isomers of [Pt(en)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> (en: H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>).

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16. When a toluene solution containing the carbene complex I shown below and excess triphenylphosphine (PPh<sub>3</sub>) is heated to reflux, compound II is formed first, and then compound III. The IR and <sup>1</sup>H NMR data for II and III are as follows:

	IR $\nu$ (CO) (cm <sup>-1</sup> )	$^{1}$ H NMR $\delta$ (ppm)
11	2038, 1958, 1906	7.62 ~ 7.41 muliplets (15), 4.19 multiplet (4)
III	1944, 1860	7.70 ~ 7.32 multiplets (15), 3.39 singlet (2)

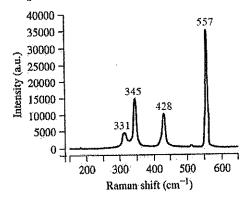
Propose the structures of II and III.

I: 
$$O \subset Br \cap O$$

$$OC - Re = C \cap O$$

$$OC \cap C \cap O$$

- 17. Copper, silver and gold crystalize in face-centered cubic (fcc) structure. (A) Sketch the fcc unit cell. (B) Calculate the packing efficiency of the fcc structure.
- 18. The Raman spectrum of AsP<sub>3</sub> shown below, exhibits four absorptions.



(A) Sketch the structure of AsP<sub>3</sub>. (B) Is the Raman spectrum consistent with the proposed structure? Support your answer by determining the number of Raman-active stretching modes for AsP<sub>3</sub>.

#### Character table

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

19. The nitrogen atom is an example of a valence  $p^3$  configuration. There are five levels associated with this configuration, with the energies shown below.

Energy (cm <sup>-1</sup> )	28839.31	28838.92	19233.18	19224.46	0
Liloigy (Oil)	<u> </u>				

Using Russell-Saunders term, assign these five energy levels.