國立中正大學
108學年度碩士班招生考試
試 題

[第3節]

系所組別	化學暨生物化學系
科目名稱	有機無機化學

—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。

科目: 無機化學

共 19 題，合計 50 分。1 – 15 題為單一選擇題，每題 2 分；
16 – 19 題為演算題，每題 5 分，請寫出演算過程。

1. How many angular nodes does the $4d_{yz}$ orbital have?
(A) 0 (B) 1 (C) 2 (D) 3 (E) 4

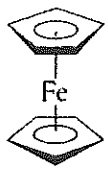
2. Write the electron configuration for V^{3+}.
(A) $[Ar]4s^23d^3$ (B) $[Ar]4s^03d^5$ (C) $[Ar]4s^23d^0$ (D) $[Ar]4s^13d^1$ (E) $[Ar]4s^03d^2$

3. On the basis of VSEPR, predict the shape of ICl_4^-.
(A) Tetrahedron (B) Octahedron (C) Square planar (D) Seesaw (E) Pyramid

4. Use molecular orbital diagram to determine the number of unpaired electrons in O_2^+.
(A) 0 (B) 1 (C) 2 (D) 3 (E) 4

5. Which one of the following oxides is the most acidic?
(A) Al_2O_3 (B) BaO (C) CO_2 (D) P_2O_5 (E) SO_3

6. Determine the point group of staggered ferrocene $(\eta^5\text{-}C_5H_5)_2Fe$.



(A) C_{5h} (B) C_{5v} (C) D_{5h} (D) D_{5d} (E) S_{10}

7. How many stereoisomers does the octahedral complex $[CoCl_2(en)(NH_3)_2]^+$ have?
(en: ethylenediamine)
(A) 2 (B) 3 (C) 4 (D) 5 (E) 6

8. Predict the form of the ^{19}F NMR spectrum of PF_3.
(For both ^{19}F and ^{31}P, $I = 1/2$, 100% natural abundance)
(A) A doublet resonance (B) A quartet resonance (C) A singlet resonance
(D) A triplet resonance (E) Three singlet resonances

9. Which one of the following elements is the most electronegative?
(A) C (B) F (C) N (D) O (E) Si

10. Which one of the following species has the smallest size?
(A) As^{3-} (B) S^{2-} (C) Cl^- (D) Ar (E) K^+

11. Which one of the following ionic compounds has the highest melting point?

(A) NaCl (B) KF (C) CaF_2 (D) CaO (E) ZnS

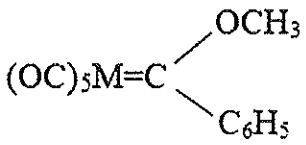
12. Determine the ground-state term for the d^3 configuration.

(A) ^2F (B) ^4F (C) ^2G (D) ^2P (E) ^4P

13. Determine the number of unpaired electrons for $[CoBr_6]^{3-}$.

(A) 0 (B) 1 (C) 2 (D) 3 (E) 4

14. On the basis of the 18-electron rule, identify the second-row transition metal for



(A) Mo (B) Tc (C) Ru (D) Rh (E) Pd

15. Which metal does play a significant role in hemoglobin ?

(A) Mn (B) Fe (C) Co (D) Ni (E) Cu

16. Metallic sodium adopts a body-centered cubic structure with density of D kg/m^3. Express the radius of sodium atom by atomic weight M, and Avogadro constant N_A?

17. Calculate the equilibrium constant of the reaction

$Au^+(aq) + 2\ CN^-(aq) \Longrightarrow [Au(CN)_2]^-(aq)$

from the following half-reaction reduction potentials:

$Au^+(aq) + e^- \Longrightarrow Au(s)$ $\quad E^\circ = +1.68$ V

$[Au(CN)_2]^-(aq) + e^- \Longrightarrow Au(s) + 2\ CN^-(aq)$ $\quad E^\circ = -0.60$ V

(hint: Nernst equation $E = E^\circ - (0.0592/n)\ logK$)

18. Determine the number of IR-active carbonyl (CO) stretching bands for *fac*-$CoCl_3(CO)_3$.

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	$(x, y)\ (R_x, R_y)$	$(x^2-y^2, xy)\ (xz, yz)$

19. Propose structural formulas for products **A** through **E** in the following reactions.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]Cl + NaH \xrightarrow{\Delta}$ **A** (the empirical formula $C_7H_6O_2Fe$)

A $\xrightarrow[\text{room temp.}]{}$ a colorless gas + a purple-brown solid **B** (the empirical formula $C_7H_5O_2Fe$)

B + I_2 ⟶ a brown solid **C** (the empirical formula $C_7H_5O_2FeI$)

C + TlC_5H_5 ⟶ a solid **D** (the empirical formula $C_{12}H_{10}O_2Fe$)

D $\xrightarrow{\Delta}$ a colorless gas + an orange solid **E** (the empirical formula $C_{10}H_{10}Fe$)

(Hint: All products must obey 18-electron rule)

The Periodic Table

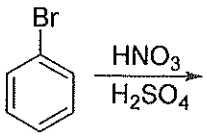
1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794	2 2A																2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.1797
11 Na 22.98977	12 Mg 24.305	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.33	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0254	89 †Ac 227.0278	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq				

*Lanthanide series	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

有機化學，共 25 題，每題 2 分，總分 50 分。

Part A. Predict the major products of the following reactions:

(1)



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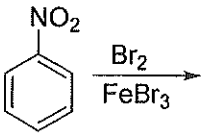

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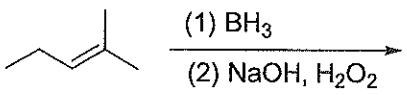

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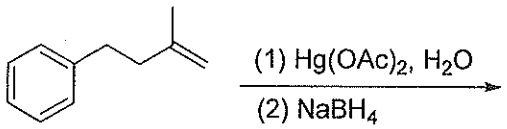

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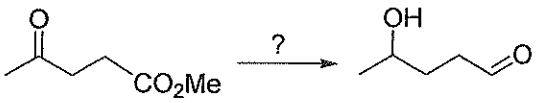

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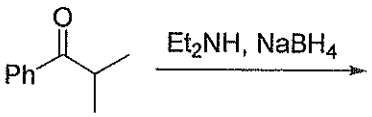

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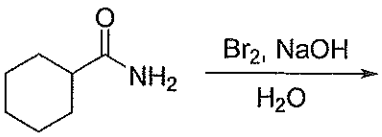
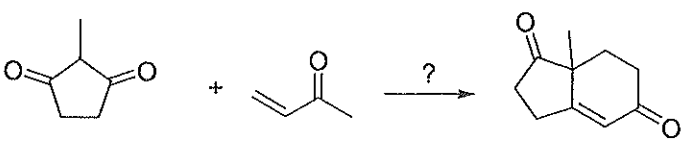


Part B. What reagent would you use to accomplish each of the following reactions? Multi-step reactions may be required for some transformations.

(8)



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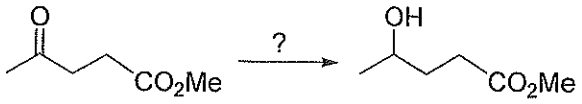

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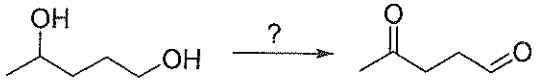

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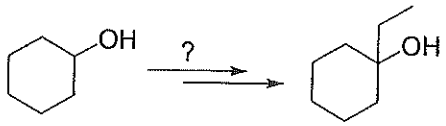

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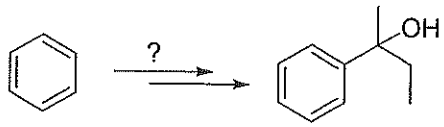

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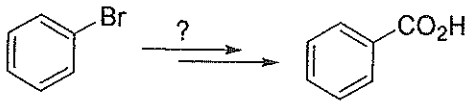

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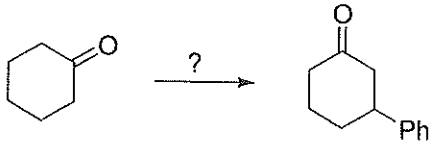

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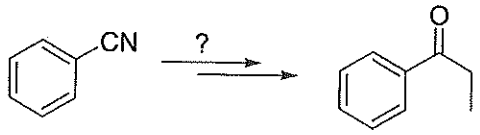
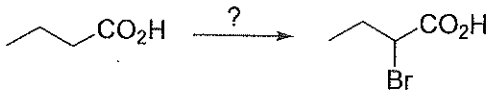


(17)



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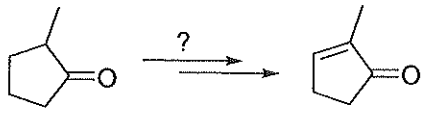
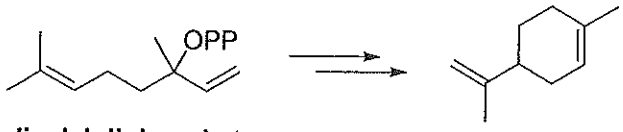


(19)

(20) Propose a mechanism for the biosynthesis of limonene from linalyl diphosphate.

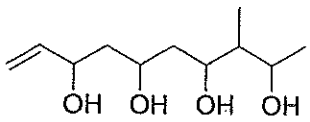


linalyl diphosphate **limonene**

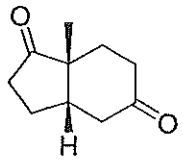
(21) Rank the following compounds in order of their expected reactivity toward S_N2 reaction: CH_3Br, CH_3OTos, $(CH_3)_3CCl$, $(CH_3)_2CHCl$.

(22) Explain your answer to the above question.

(23) How many stereoisomers of the following compound are possible in principle?



(24) Assign the absolute configuration to the chirality center in the following molecule.



(25) An unknown compound, $C_8H_{10}O_2$, has an IR absorption at 1750 cm^{-1} and the ^{13}C NMR absorption peaks as following. ^{13}C ($CDCl_3$, 100 MHz NMR): δ 219.5 (C), 43.7 (CH_2), 36.2 (CH). Please prose a structure for the compound.