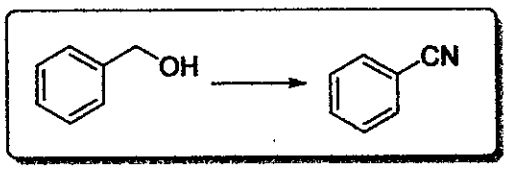
第一部份：單選題 ※ 注意：請用 2B 鉛筆作答於答案卡，並先詳閱答案卡上之「畫記說明」。
有機化學（每題 2 分）

1. Which of the following compound is **least basic**?
(A) aniline (B) pyridine (C) triethylamine (D) imidazole (E) pyrrole

2. Which of the following compound(s) can **NOT** be deprotonated by lithium diisopropylamide?
(A) 2,4-pentanedione (B) 1-pentyne (C) cyclopentanol (D) 1-pentene (E) cyclopentanone

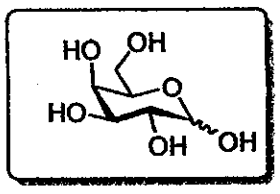
3. In a typical ^{13}C NMR spectrum, how many **^{13}C signals** can you observe in **benzyl benzoate**?
(A) 7 (B) 9 (C) 10 (D) 12 (E) none of above

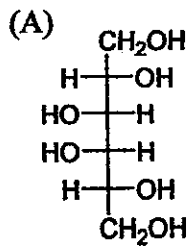
4. Which following scheme can complete the boxed transformation?

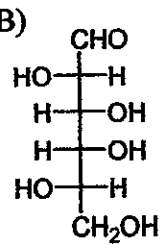


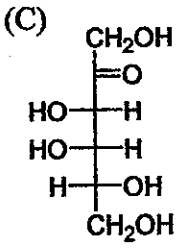
(A) (i) PBr_3; (ii) NaCN, DMF
(B) (i) HBr; (ii) Mg, THF; (iii) NaCN
(C) (i) PDC, CH_2Cl_2; (ii) NaCN, DMF
(D) (i) $KMnO_4$; (ii) $SOCl_2$; (iii)NH_3; (iv) P_4O_{10}
(E) (i) MnO_2; (ii) NH_3; (iii) $NaBH_4$; (iv) $NaNO_2$, HCl; (v) CuCN

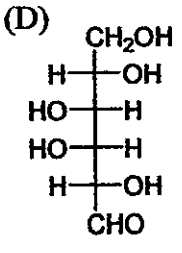
5. Which is the following open-chain form the boxed compound has?

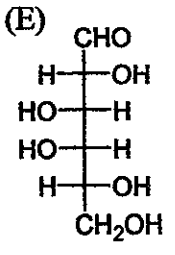


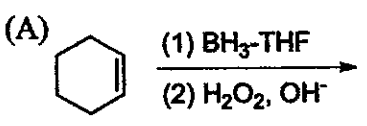
(A) 

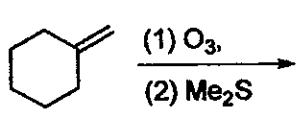
(B) 

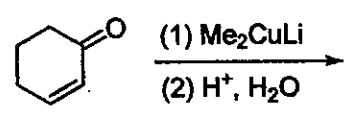
(C) 

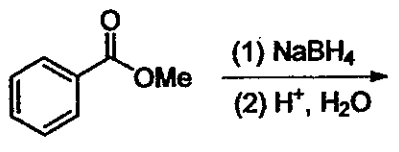
(D) 

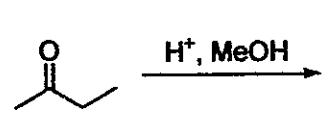
(E) 

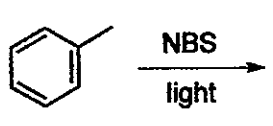
6. Which is the following reaction does give **alcohol** as the major product?
(A) 

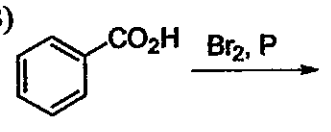
(B) 

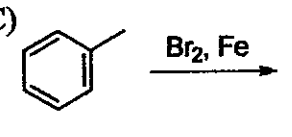
(C) 

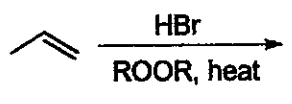
(D) 

(E) 

7. Which is the following reaction does **NOT** give a major **substitution** bromide product?
(A) 

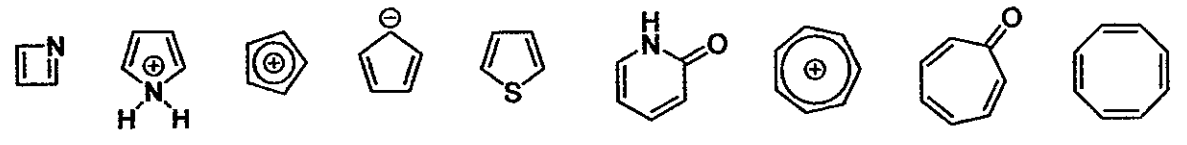
(B) 

(C) 

(D) 

(E) 

8. How many of the following species are **aromatic**?



(A) 4 (B) 5 (C) 6 (D) 7 (E) 8

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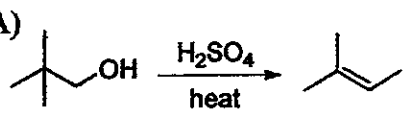
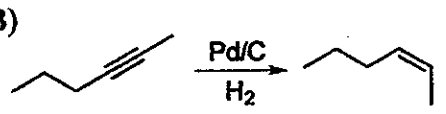
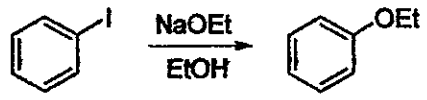
9. Which of the following reaction can afford the major product as shown?

(A) 

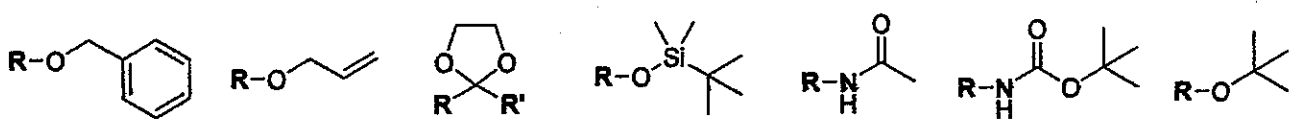
(B) 

(C) 

(D) 

(E) 

10. How many of the following protecting groups can be **resistant** to the lithium aluminium hydride?

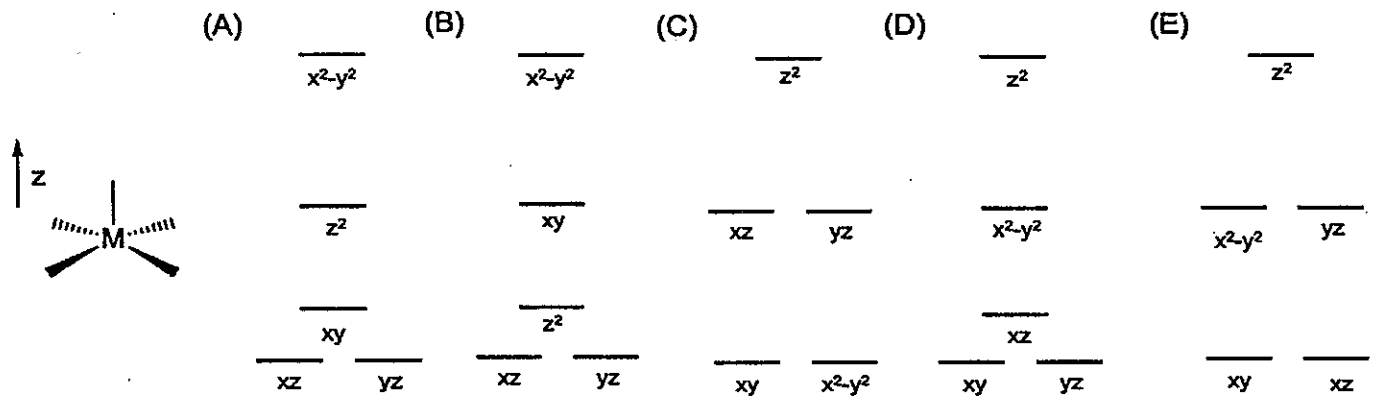


(A) 2　(B) 3　(C) 4　(D) 5　(E) 6

無機化學（每題 3 分）

Single choose. Please select the most appropriate answer for the following questions. (3 points each, total 15 points)

11. Which is the correct d-orbital energy diagram of a complex in a square pyramidal geometry.



12. Which of the following descriptions about single crystal X-ray diffraction (SXRD) is *NOT* correct?

(A) Practically speaking, SXRD is a useful tool to determine the oxidation state of metal complexes.
(B) In general, SXRD can be used to determine the position of all atoms except for hydrogen atoms.
(C) With the same space group, a larger unit cell in the direct space will show a smaller unit cell in the reciprocal space.
(D) Both molecules and single crystals can have C_5 proper axes.
(E) None of the above.

13. How many of the following molecules do *NOT* have an inversion center?
(a) NH_3 (b) C_2H_2, (c) C_6H_6 (d) BF_3 (e) CH_4 (f) $[PtCl_4]^{2-}$ (g) S_8 (h) C_3H_4 (Allene) (i) C_{60} (j) SF_6

(A) 3
(B) 5
(C) 6
(D) 7
(E) 9

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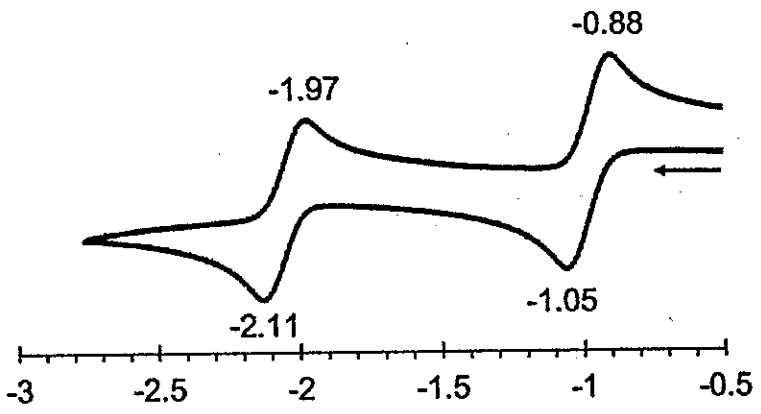
14. According to the hard-soft acid base theory, how many of the following reactions will go right? (i.e. K_{eq} > 1)

(a) $NH_3 + CaF^+ \rightleftharpoons Ca(NH_3)^{2+} + F^-$
(b) $Ag(CN)^{2-} + 2\ Cl^- \rightleftharpoons AgCl^{2-} + 2\ CN^-$
(c) $[Fe(dppe)_3]^{3+} + 3$ bipy $\rightleftharpoons [Fe(bipy_3)]^{3+} + 3$ dppe
(d) $AlI_3 + 3NaF \rightleftharpoons AlF_3 + 3NaI$
(e) $CoF_2 + HgBr_2 \rightleftharpoons CoBr_2 + HgF_2$
(f) $Cu(OSMe_2) \rightleftharpoons Cu(SOMe_2)$
(g) $CuI_2 + 2CuF \rightleftharpoons CuF_2 + 2CuI$
(h) $Me_3P\text{-}BBr_3 + Me_3N\text{-}BF_3 \rightleftharpoons Me_3P\text{-}BF_3 + Me_3N\text{-}BBr_3$
(i) $H_3B\text{-}CO + BBr_3 \rightleftharpoons H_3B + Br_3B\text{-}CO$
(j) $TlF + NaI \rightleftharpoons TlI + NaF$
(k) $CH_3HgBr + HCl \rightleftharpoons CH_3HgCl + HBr$

Unless otherwise stated, assume gas-phase or hydrocarbon solution at 298K
(A)9 (B) 8 (C) 7 (D) 6 (E) 5

15. The cyclic voltammogram of a boron based complex (LBX_2) and a table of selected reductants are shown below. How many of the following statements are correct?



reductant	Potentials (V)[a]
$[C_{10}H_8]^-$	-2.65
Na(Hg)	-1.91
$[FeCp(\eta\text{-}C_6Me_6)]$	-1.61
$[CoCp^*_2]$	-1.49
$[CoCp_2]$	-0.88
$[Cr(\eta\text{-}C_6H_6)_2]$	-0.70
$[FeCp_2]$	0.45

a: in THF solution (vs SCE)

(a) $[LBX_2]^{2-}$ can be generated by adding 2 equiv. of $[C_{10}H_8]^-$
(b) $[LBX_2]^{2-}$ can be generated by adding 2 equiv. of $[FeCp(\eta\text{-}C_6Me_6)]$
(c) $[LBX_2]^{2-}$ can be generated by adding 1 equiv. of $[CoCp^*_2]$ and 1 equiv. of Na(Hg)
(d) $[LBX_2]^-$ can be generated by adding 1 equiv. of $[Cr(\eta\text{-}C_6H_6)_2]$
(e) $[LBX_2]^-$ can be generated by adding 2 equiv. of $[CoCp^*_2]$
(f) $[LBX_2]^-$ can be generated by adding 1 equiv. of $[CoCp_2]$
(g) $[LBX_2]^-$ can be generated by adding 2 equiv. of $[FeCp_2]$

(A)6 (B) 5 (C) 4 (D) 3 (E) 2

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第二部份：問答題 ※ 注意：請於試卷內之「非選擇題作答區」依序作答，並應註明作答之部份及題號。

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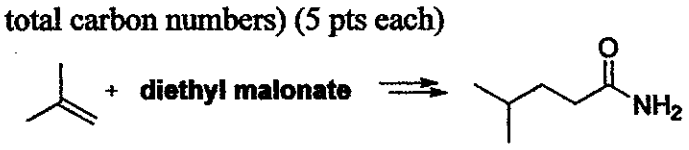
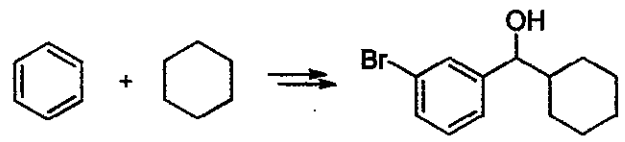
1. Using two starting materials shown, provide **synthetic schemes** and **intermediates** to prepare the products. (Hint: Notice the total carbon numbers) (5 pts each)

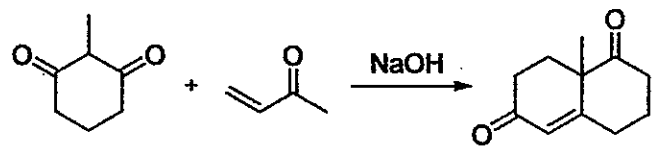
(A)



(B)

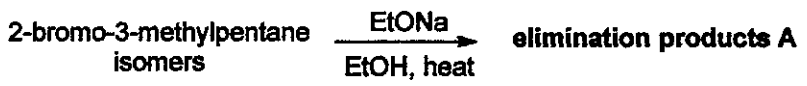


2. Write the step-by-step **mechanism** to account for the product of the following reaction: (6 pts)



3. (A) Draw all possible stereoisomers of 2-bromo-3-methylpentane and identify their stereochemical relationships. (6 pts)

(B) 2-bromo-3-methylpentane isomers undergo elimination under the following condition. Provide the major **elimination products A** of each isomer. (4 pts)



(C) 2-bromo-3-methylpentane undergoes elimination under **condition B** to generate the **major product C** as **the constitutional isomer** of elimination products **A**. Provide and explain briefly a possible **condition B** and **product C**. (4 pts)

無機化學 Please provide a short answer for the following questions. (total 35 points)

4. (10 points) Construct a molecular orbital diagram for a planar BH_3 molecule. Please include the following features in your MO diagram.
   (i) On an energy diagram draw out the energies of the fragment orbitals.
   (ii) Which interactions between the fragment orbitals are allowed by symmetry?
   (iii) Give the form and relative energies of the MOs.

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5. (total 20 points) Open-shell molecules such as radicals usually play crucial roles in chemical transformations due to their high energies and high reactivities. Electron spin resonance (ESR) spectroscopy is one of the widely used spectroscopic techniques for detecting the open-shell molecules. Please answer the following questions related to ESR spectroscopy and radical chemistry. (Note: you need to include necessary explanations for your answers)

(a) (5 points) Use an energy level diagram to describe the basic principles of ESR spectroscopy for a spin 1/2 system.

(b) (10 points) Imagining there is an organic molecule having two unpaired electrons, and the coupling constant between the two unpaired electrons is J. Please draw ESR spectrum when

(I) $J = 0$

(II) $J < 0$ (antiferromagnetic couple)

(III) $J > 0$ (ferromagnetic couple)

Please provide your explanations next to each spectrum.

(c) (5 points) In some cases, the energy gap between the singlet state and the triplet state of a diradical molecule is small. Therefore, the high-energy state can be easily populated by thermal energy resulted in a spin-crossover phenomenon.

(I) Design an experiment to determine which state, singlet state or triplet state, is the ground state.

(II) What data would you expect to obtain from the experiment you designed in section (I)? How would you interpret the data?

Note: You only need to provide qualitative descriptions, and you can use any experimental techniques.

6. (total 5 points) For the reaction

$$2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

the currently accepted mechanism is

$$\text{step 1} \qquad 2\,NO_{(g)} \longrightarrow N_2O_{2(g)}$$

$$\text{step 2} \qquad N_2O_{2(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

(a) (2 points) Determine which step is the slow step.

(b) (3 points) Explain clearly why you chose the reaction as the slow step.
You may use Lewis structures to help in your explanation.

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