

# 國立中山大學 109 學年度 碩士暨碩士專班招生考試試題

科目名稱：有機化學及無機化學【化學系碩士班】

## —作答注意事項—

考試時間：100 分鐘

- 考試開始鈴響前不得翻閱試題，並不得書寫、劃記、作答。請先檢查答案卷（卡）之應考證號碼、桌角號碼、應試科目是否正確，如有不同立即請監試人員處理。
- 答案卷限用藍、黑色筆(含鉛筆)書寫、繪圖或標示，可攜帶橡皮擦、無色透明無文字墊板、尺規、修正液（帶）、手錶(未附計算器者)。每人每節限使用一份答案卷，不得另攜帶紙張，請衡酌作答。
- 答案卡請以 2B 鉛筆劃記，不可使用修正液（帶）塗改，未使用 2B 鉛筆、劃記太輕或污損致光學閱讀機無法辨識答案者，其後果由考生自行負擔。
- 答案卷（卡）應保持清潔完整，不得折疊、破壞或塗改應考證號碼及條碼，亦不得書寫考生姓名、應考證號碼或與答案無關之任何文字或符號。
- 可否使用計算機請依試題資訊內標註為準，如「可以」使用，廠牌、功能不拘，唯不得攜帶具有通訊、記憶或收發等功能或其他有礙試場安寧、考試公平之各類器材、物品（如鬧鈴、行動電話、電子字典等）入場。
- 試題及答案卷（卡）請務必繳回，未繳回者該科成績以零分計算。
- 試題採雙面列印，考生應注意試題頁數確實作答。
- 違規者依本校招生考試試場規則及違規處理辦法處理。

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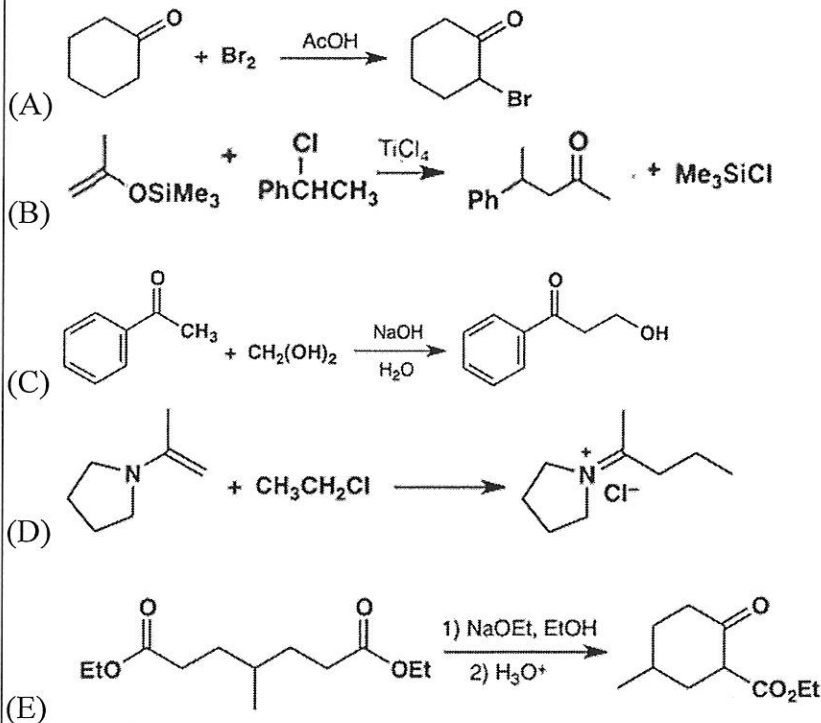
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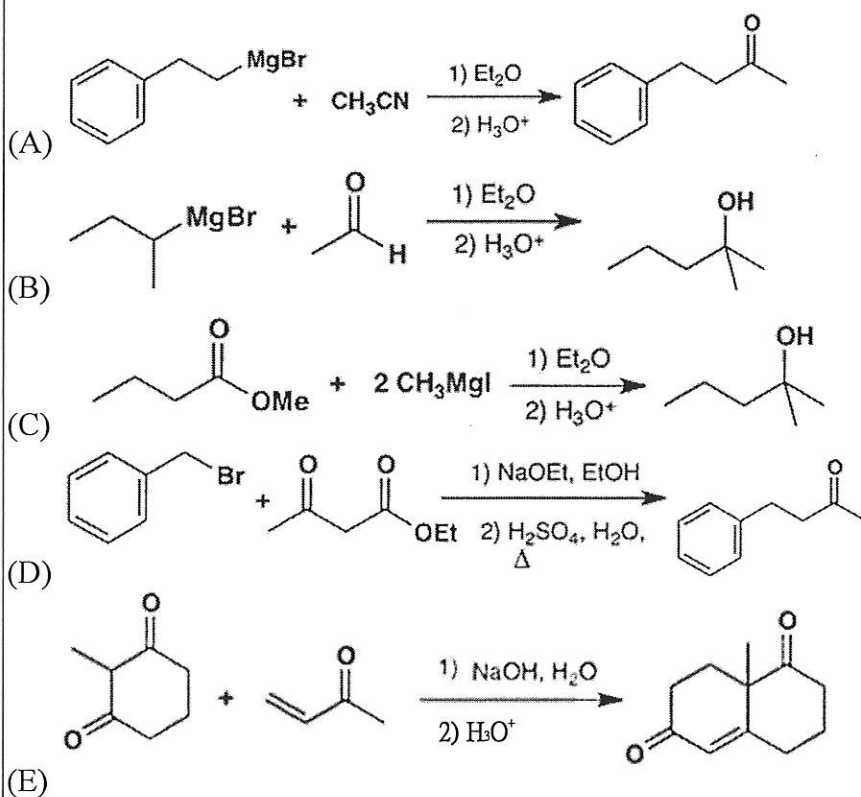
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一、單選題 (每題 3 分, 總計 66 分)

1. Which of the following will **not** be the major product for the following reactions below?



2. Which reaction will **not** give the desired product?



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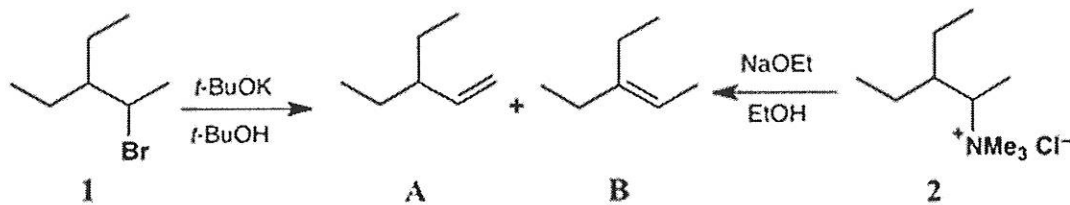
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3. Which reaction conditions are **not** appropriate for the following transformation?



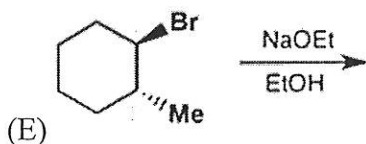
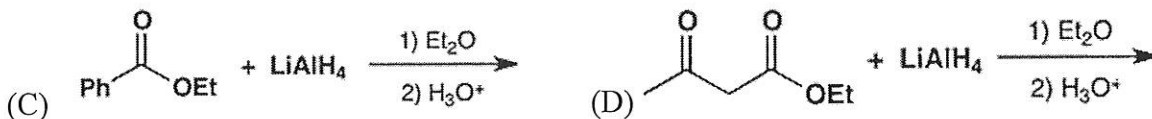
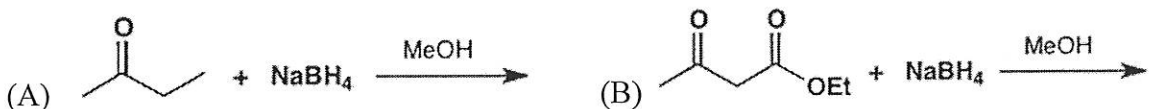
- (A) Zn (Hg) / HCl                      (B) H<sub>2</sub>NNH<sub>2</sub> / NaOH                      (C) NaNH<sub>2</sub>, NH<sub>3</sub>  
 (D) HSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH / H<sup>+</sup>, then H<sub>2</sub> / Ni                      (E) 1, NaBH<sub>4</sub>; 2. TsCl, 3. LiAlH<sub>4</sub>

4. Which of the following statements best indicates the most probable outcome?

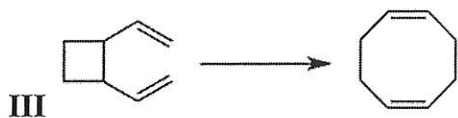
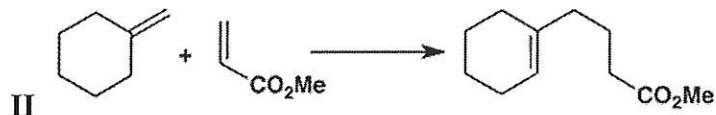
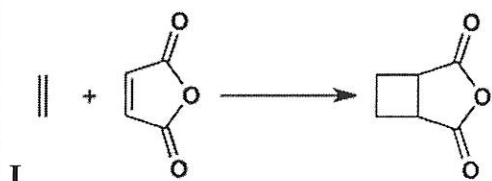


- (A) 1 and 2 give A as major product                      (B) 1 and 2 give B as major product  
 (C) 1 give A and 2 give B                      (D) 1 give B and 2 give A                      (E) 1 and 2 give A and B complex mixture

5. Which of the following reactions will **not** give rise to racemic mixture or chiral product?

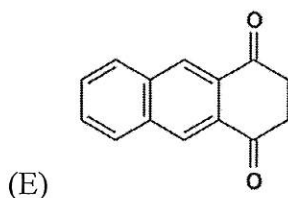
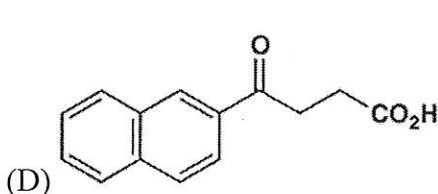
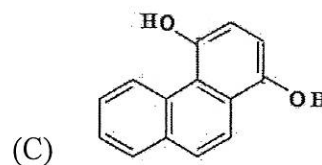
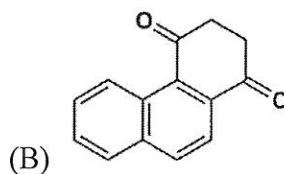
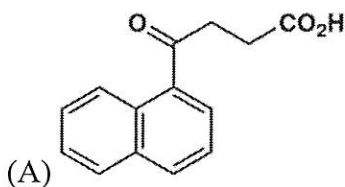
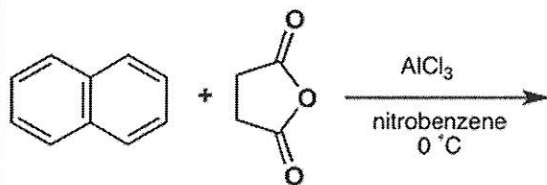


6. Which of the following reactions is thermally allowed?

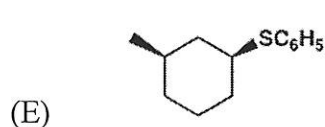
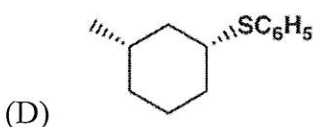
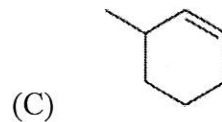
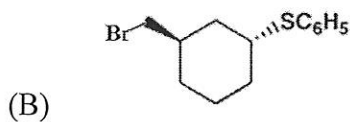
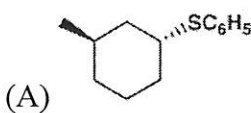
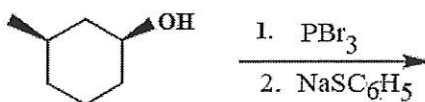


- (A) I, II      (B) II, III      (C) III, IV      (D) II, III, IV      (E) IV

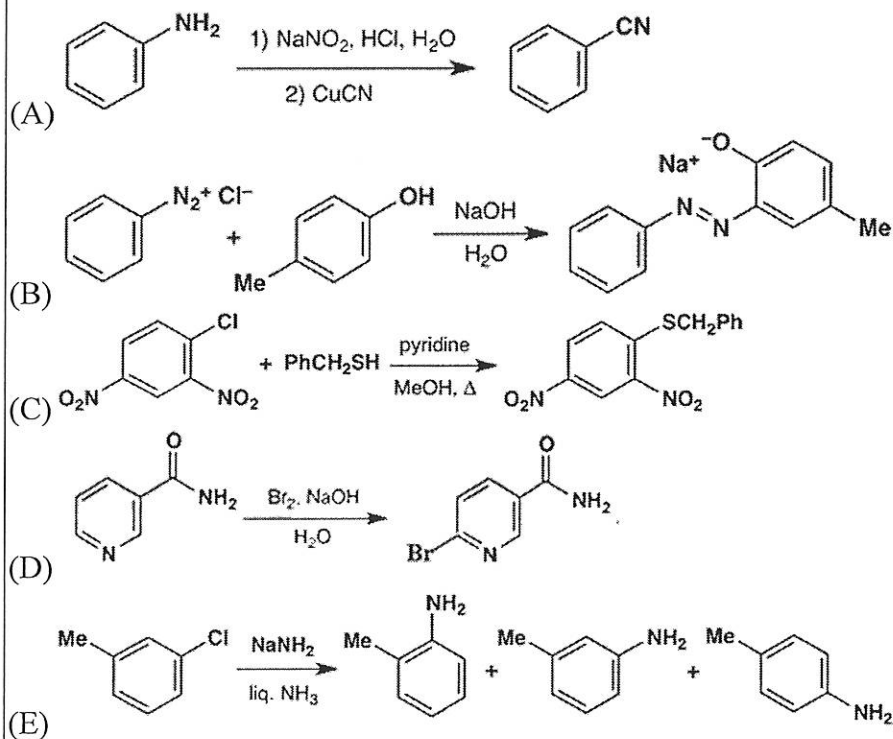
7. Which is the **most** probable main product of the following reaction?



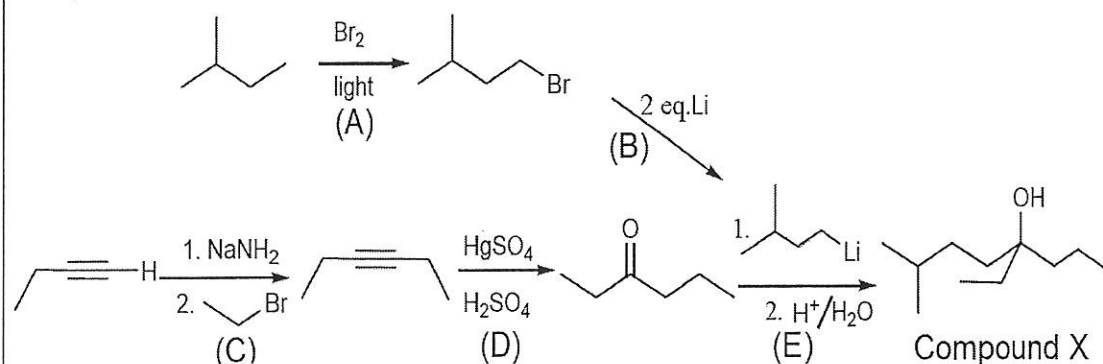
8. Which is the main product of the following reaction?



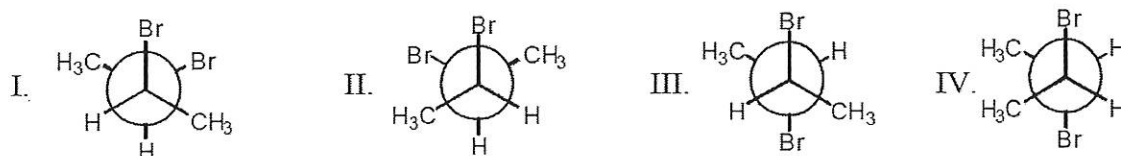
9. In which of the following reaction give the **incorrect** desire product?



10. Below is a propose synthesis of compound X. Which step would **not** work.



11. Which of the following Newman projections represents *meso*-2,3-dibromobutane?



(A) I (B) II (C) III (D) IV (E) I and IV

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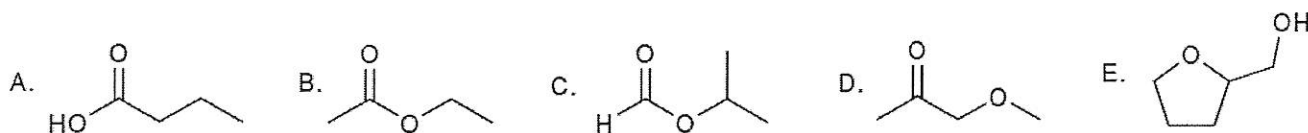
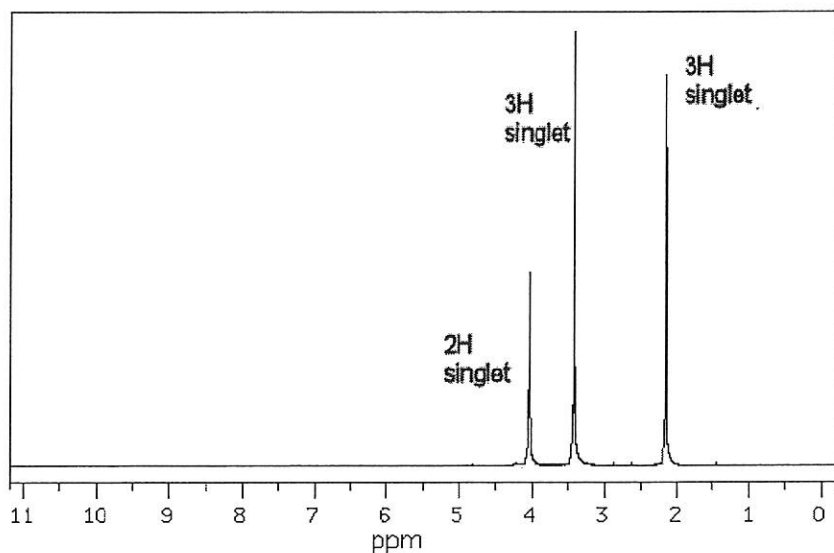
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12. Which structure shown below is consistent with the following NMR spectrum?



13. What are the effective nuclear charge  $Z^*$  on a 5f, 6d, and 7s in a uranium atom?

- (A) 14.3, 2.0, 3.0 (B) 15.3, 3.0, 2.0  
(C) 12.3, 2.0, 2.0 (D) 13.3, 3.0, 3.0

14. The reaction  $A \rightarrow B + C$  is known to be zero order in A with a rate constant of  $4.8 \times 10^{-2} \text{ mol/L} \cdot \text{s}$  at  $25^\circ\text{C}$ . An experiment was run at  $25^\circ\text{C}$  where  $[A]_0 = 2.0 \text{ M}$ . What is the concentration of B after 4.0 s?

- (A) 1.8 M (B)  $5.5 \times 10^{-1} \text{ M}$  (C)  $1.1 \times 10^{-1} \text{ M}$  (D)  $1.9 \times 10^{-1} \text{ M}$

15. For  $\text{As}_2\text{P}_2$ , what are the irreducible representations for experimentally observed Raman bands?

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	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	$y, R_x$	$yz$

- (A)  $3A_1 + A_2 + B_1 + B_2$  (B)  $2A_1 + 2A_2 + B_1 + B_2$  (C)  $2A_1 + A_2 + 2B_1 + B_2$   
(D)  $A_1 + A_2 + B_1 + 3B_2$

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16. What is SALC of  $b_{2u}$  molecular orbital consisted of four p orbitals in cyclobutadiene?

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

(A)  $\chi_1 + \chi_2 + \chi_3 + \chi_4$

(B)  $\chi_1 + \chi_2 - \chi_3 - \chi_4$

(C)  $\chi_1 - \chi_2 + \chi_3 - \chi_4$

(D)  $\chi_1 - \chi_2 - \chi_3 - \chi_4$

17. What is the enthalpy of formation of MgO, which crystallizes in the NaCl lattice (use the Born-Haber cycle to calculate). Use these data in the calculation:  $O_2$  bond energy = 494 kJ/mol;  $\Delta H_{sub}(Mg) = 37$  kJ/mol. Second ionization energy of Mg = 1451 kJ/mol; second electron affinity of O = -744 kJ/mol.  
 (A) 2352 kJ mol<sup>-1</sup> (B) -3934 kJ mol<sup>-1</sup> (C) -1341 kJ mol<sup>-1</sup> (D) 1341 kJ mol<sup>-1</sup>

18. The half-life of <sup>14</sup>C is 5730 years. A sample taken for radiocarbon dating was found to contain 56 percent of its original <sup>14</sup>C. What was the age of the sample? (Radioactive decay of <sup>14</sup>C follows first-order kinetics.)  
 (A)  $2.2 \times 10^3$  (B)  $3.1 \times 10^2$  (C)  $4.8 \times 10^3$  (D)  $1.1 \times 10^4$

19. Which of the following is the free ion terms of  $d^2$  configuration?  
 (A)  $^3G, ^1F, ^1D, ^3P, ^1S$  (B)  $^1G, ^3F, ^1D, ^3P, ^1S$  (C)  $^3G, ^1F, ^1D, ^1P, ^3S$   
 (D)  $^1G, ^1F, ^1D, ^3P, ^3S$

20. Which is the correct splitting pattern of d orbitals for  $[CuCl_5]^{3-}$  energetically?  
 (A)  $d_{xz} = d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$  (B)  $d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$   
 (C)  $d_{xz} = d_{yz} < d_{x^2-y^2} = d_{xy} < d_{z^2}$  (D)  $d_{xy} = d_{x^2-y^2} < d_{xz} = d_{yz} < d_{z^2}$

21. The <sup>14</sup>N and <sup>15</sup>N derivatives of TpOs(NS)Cl<sub>2</sub> [Tp = hydrotris(1-pyrazolyl)borate, a tridentate ligand] have been prepared. The <sup>14</sup>N derivative has a nitrogen-sulfur stretch at 1284 cm<sup>-1</sup>. Predict the N—S stretch for the <sup>15</sup>N derivative.  
 (A) 1314 cm<sup>-1</sup> (B) 1254 cm<sup>-1</sup> (C) 1224 cm<sup>-1</sup> (D) 1194 cm<sup>-1</sup>

22. Which of the following step is NOT included in the hydroformylation (oxo) process?  
 (A)  $\beta$  elimination (B) Addition of CO  
 (C) Alkyl migration (D) 1,2-insertion

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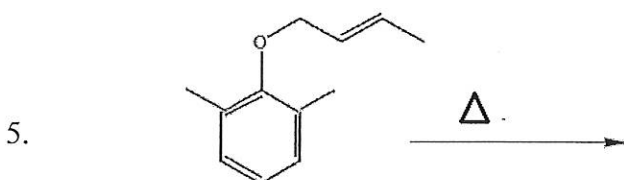
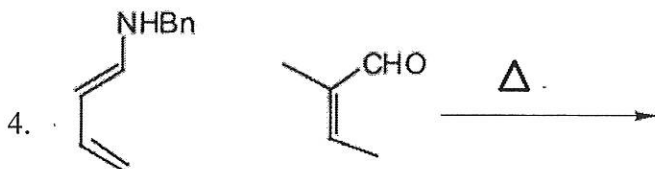
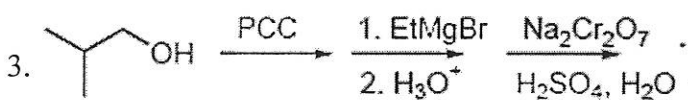
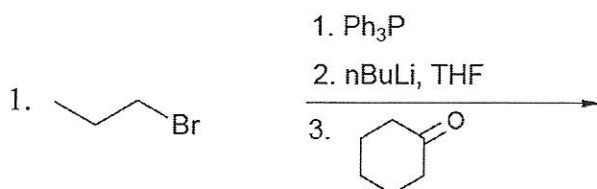
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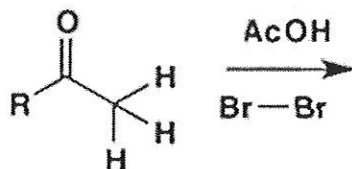
二、(每題 2 分，總計 10 分)

Please give the product for the reaction below, illustrating the stereochemistry of the product when necessary.



三、(每題 4 分，總計 4 分)

1. Shows a mechanism for the  $\alpha$ -bromination of a methyl ketone with bromine in acetic acid. (Include all the lone-pair of electrons)



四、(每題 10 分，總計 20 分)

1. Please give the step-by-step reaction mechanism of water gas shift reaction using  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  as a homogeneous catalyst.



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2. (a) Please construct the molecular orbital diagram of CO step by step with orbital contour for each molecular orbital (Potential Energy of C(2s): -19.43; C(2p): -10.66; O(2s): -32.38; O(2p): -15.85; H(1s): -13.61 eV)
- (b) Briefly explain the information provided by its photoelectron spectrum of CO including the meaning of fine structure of photoelectron spectrum in terms of bonding and antibonding characters as well as the difference of the intensity in terms of overlapping of vibrational wavefunction

