

國立高雄大學九十七學年度研究所碩士班招生考試試題

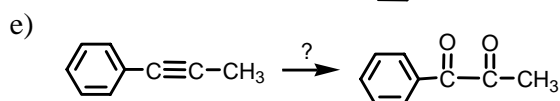
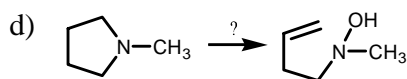
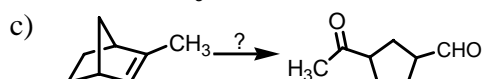
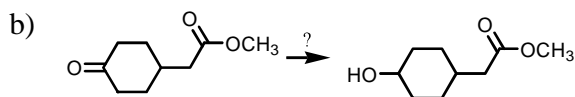
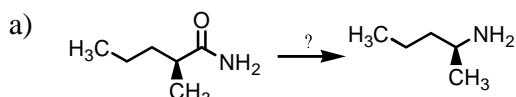
科目：綜合化學(I)  
考試時間：100 分鐘

系所：  
應用化學系碩士班  
本科原始成績：100 分

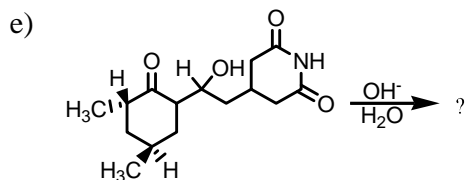
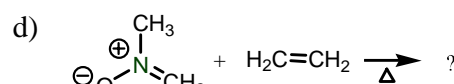
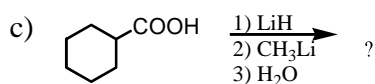
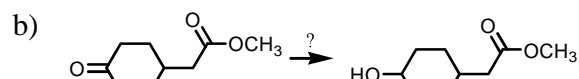
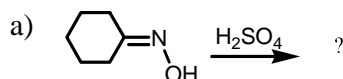
是否使用計算機：是

**PART I: Organic Chemistry ; Total = 50 points**

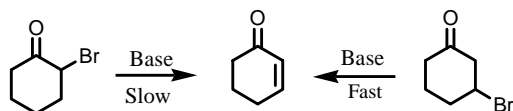
1. Predict the major organic product formed in each following reaction. (10 pts)



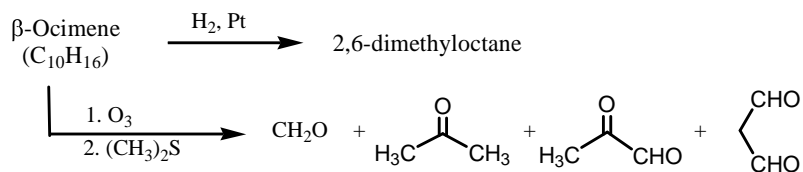
2. Give some proper reagents that bring the following reaction occurrence. (10 pts)



3. Treatment of both  $\alpha$ - and  $\beta$ -bromoketones with base results in loss of HBr to form  $\alpha,\beta$ -unsaturated ketones. However, the former react much more slowly and require much stronger bases. Account for this difference in reactivity by providing a complete analysis of both reaction mechanisms. (6 pts)



4.  $\beta$ -Ocimene is a natural product with a pleasant odor. Based on the information below, deduce the structure of  $\beta$ -ocimene. (4 pts)



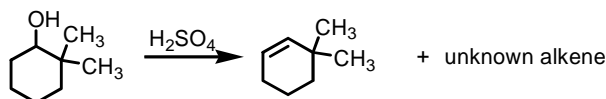
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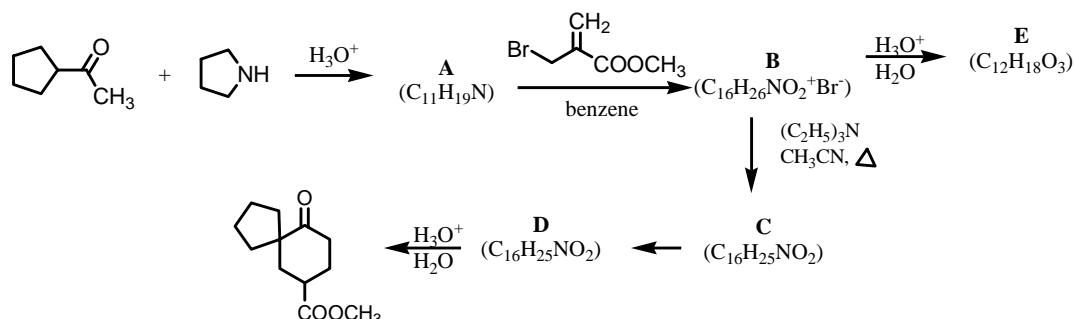
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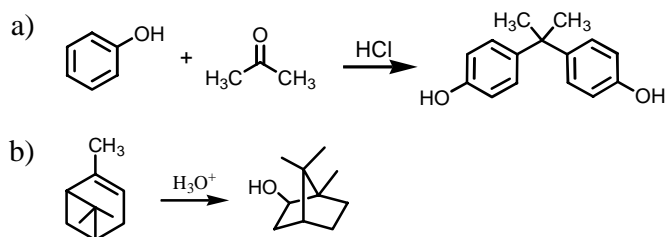
5. Upon treatment with acid, 2,2-dimethylcyclohexanol undergoes dehydration to form 3,3-dimethylcyclohexene and another alkene that exhibits only four unique signals in the  $^{13}\text{C}$  NMR spectrum yet has a mass of 110, corresponding to the formula  $\text{C}_8\text{H}_{14}$ . Assign a structure to this product, and account for its formation with a detailed reaction mechanism. (4 pts)



6. provide exact intermediates A-E for the following reactions (10 pts)



7. Suggest a convenient method for carrying out the following syntheses. (6 pts)



PART II: Inorganic Chemistry ; Total = 50 points

- Provide a concise but thorough explanation of the following (10 points)
  - Trans effect
  - Valence bond theory
  - n-type semiconductor
  - 18 electrons rule
- How many spherical nodes dose  $4d_{x^2-y^2}$  orbital have? (2 points)
  - How many angular nodes dose  $4d_{x^2-y^2}$  orbital have? (2 points)

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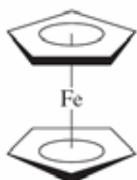
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3. Determine the point groups for (9 points)

(a) Cyclohexane (chair conformation)

(b)  $\text{BrF}_5$  (c)  $\text{Fe}(\text{C}_5\text{H}_5)_2$  (staggered)



4. The  $d^2$  ions  $\text{CrO}_4^{4-}$ ,  $\text{MnO}_4^{3-}$ ,  $\text{FeO}_4^{2-}$ , and  $\text{RuO}_4^{2-}$  have been reported. (9 points)

(a) Which of these has the largest value of  $\Delta_t$ ? The smallest? Explain briefly.

(b) Of the first three, which ion has the shortest metal-oxygen bond distance? Explain briefly.

(c) The charge-transfer transitions for the first three complexes occur at 43000, 33000, and 21000  $\text{cm}^{-1}$ , respectively. Are these more likely to be ligand to metal or metal to ligand charge-transfer transitions? Explain briefly.

5.  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  have  $D_{4d}$  symmetry. How many IR-active carbonyl stretching bands would you predict for these compounds? (10 points)

$D_{4d}$	$E$	$2S_8$	$2C_4$	$2S_8^3$	$C_2$	$4C_2'$	$4\sigma_d$		
$A_1$	1	1	1	1	1	1	1	$R_z$	$x^2 + y^2, z^2$
$A_2$	1	1	1	1	1	-1	-1		
$B_1$	1	-1	1	-1	1	1	-1		
$B_2$	1	-1	1	-1	1	-1	1	$z$	$(x^2 - y^2, xy)$
$E_1$	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0		
$E_2$	2	0	-2	0	2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_3$	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0		

6. Of the donor-acceptor complexes  $(\text{CH}_3)_3\text{N-SO}_3$  and  $\text{H}_3\text{N-SO}_3$  in the gas phase (8 points)

(a) Which has the longer N-S bond? Explain briefly.

(b) Which has the larger N-S-O angle? Explain briefly.