

國立中山大學九十三年學年度博士班招生考試試題

科目：綜合化學【化學系】

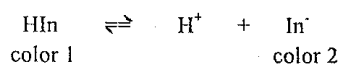
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有機化學、無機化學、分析化學、物理化學

[四科任選二科作答]

分析化學

1. The acid/base indicator HIn undergoes the following reaction in dilute aqueous solution:



The following absorbance data were obtained for a  $5.00 \times 10^{-4}$  M solution of HIn in 0.1 M NaOH and 0.1 M HCl. Measurements were made at a wavelength of 485 nm and 625 nm with 1.00-cm cells.

0.1 M NaOH	$A_{485} = 0.052$	$A_{625} = 0.823$
0.1 M HCl	$A_{485} = 0.454$	$A_{625} = 0.176$

In the NaOH solution essentially all indicator is present as  $\text{In}^-$ ; in the acidic solution, it is essentially all in the form of HIn.

- Calculate molar absorptivities for  $\text{In}^-$  and HIn at 485 and 625 nm.
- Calculate the acid dissociation constant for the indicator if a pH 5.00 buffer containing a small amount of the indicator exhibits an absorbance of 0.472 at 485 nm and 0.351 at 625 nm.
- What is the pH of a solution containing a small amount of the indicator that exhibits an absorbance of 0.530 at 485 nm and 0.216 at 625 nm? (20%)

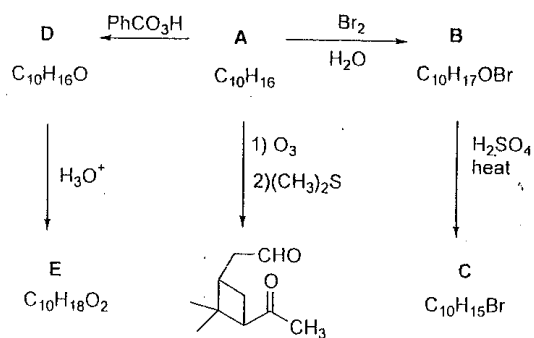
2. The fact that atoms and molecules absorb light is the basis for many different spectroscopic techniques in chemical analysis. List and discuss briefly ten different ways through which absorption can be detected. In each case indicate what signal is measured and how the signal is related to atomic or molecular concentration. (30%)

有機化學

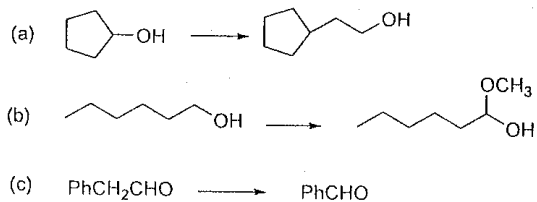
1. Define the following terms. (you can illustrate the term by giving example) (15 pts)

- (a) Carbene (b) Acyclic compound (c) Hydride reagent  
(d) Antiaromatic compound (e) Diastereomers

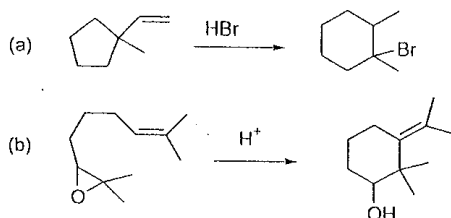
2. What are the structures of A-E below? (10 pts)



3. Devise methods for accomplishing the following transformations. (15 pts)



4. Propose a reasonable mechanism for each of the following reactions. (10 pts)

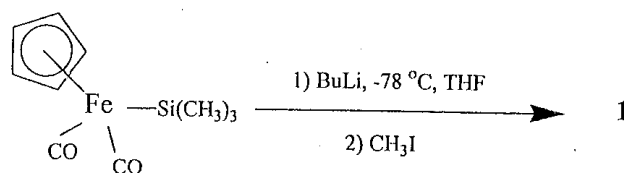


Inorganic Chemistry

(1) (25 points) Determine the IR- and Raman-active representations for the five in-plane vibrations of the trans-N<sub>2</sub>F<sub>2</sub> molecule.

C <sub>2h</sub>	E	C <sub>2</sub>	i	σ <sub>h</sub>		
A <sub>g</sub>	1	1	1	1	Rz	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
B <sub>g</sub>	1	-1	1	-1	Rx, Ry	xy
A <sub>u</sub>	1	1	-1	-1	z	xz, yz
B <sub>u</sub>	1	-1	-1	1	x, y	

(2) (25 points) Give the product and propose a mechanism for the following transformation:



Spectral data for 1:

<sup>1</sup>H NMR (δ, CS<sub>2</sub>): 4.67-4.90 (m, 4H); 0.31 (s, 9H); 0.18 (s, 3H)

IR (cm<sup>-1</sup>, in CHCl<sub>3</sub>): 1991, 1937

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物理化學

1. (25%) For 1s orbital,  $R_{1,0} = 2(Z/a_0)^{3/2} e^{-Zr/a_0}$ . Please find the radial distribution function of 1s orbital,  $P(r)$ . Calculate the most probable radius at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom  $\text{He}^+$ . Note :  $a_0 = 52.9 \text{ pm}$ .

2. (25%) The NO group in N,N-dimethylnitrosamine,  $(\text{CH}_3)_2\text{N}-\text{NO}$ , rotates and, as a result, the magnetic environments of the two  $\text{CH}_3$  groups are interchanged. In a 600MHz NMR spectrometer the two  $\text{CH}_3$  resonances are separated by 390 Hz. At what rate of interconversion will the resonance collapse to a single line?