高雄醫學大學九十六學年度博士班招生考試　儀器分析(甲)　試題 第一頁

1. Define (a) Nernst diffusion, (b) Nernst equation, (c) Stokes shift (9%)
2. Predict the order of elution of (a) n-hexane, n-hexanol and benzene in a normal-phase separation, (b) ethyl acetate, diethyl ether and nitromethane in a reversed-phase separation.(6%)
3. Describe a major advantage of micellar electrokinetic capillary chromatography over conventional liquid chromatography. (6%)
4. Sketch a photometric titration curve for the titration of $Sn^{2+}$ with $MnO_4^-$. What color radiation should be used for this titration? Explain. (6%)
5. A 2.00-mL urine sample was treated with molybdenum blue reagents to produce a species absorbing at 820 nm, after which the sample was diluted to 100.00 mL. A 25.00-mL aliquot gave an absorbance of 0.428. Addition of 1.00 mL of a solution containing 0.0500 mg of phosphate to a second 25.0-mL aliquot gave an absorbance of 0.517. Use these data to calculate the number of milligrams of phosphate per milliliter of the sample. (7%)
6. What are the principal advantages and principal limitations of the following detectors: (a) electron capture, (b) flame-ionization and (c) thermal conductivity, as used in gas chromatography? (12%)
7. List the differences in properties and roles of the mobile phases in gas and liquid chromatography. How do these differences influence the characteristics of the two methods? (10%)
8. Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence? (8%)
9. What are the advantages of performing voltammetry with ultramicroelectrodes? (8%)
10. Why are stripping methods more sensitive than other voltammetric procedures? (8%)
11. The spectrum in Fig. 1 was obtained for a liquid with an empirical formula of $C_3H_6O$. Identify the structure and explain. (6%)

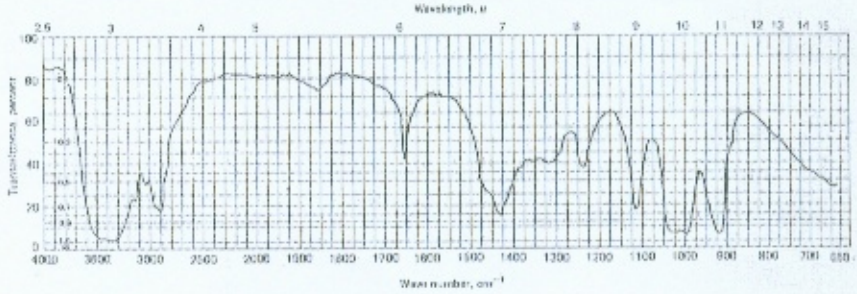



Fig. 1

12. Identify the ions responsible for the four peaks having greater masses than the $M^+$ peak in Fig. 2. (4%)

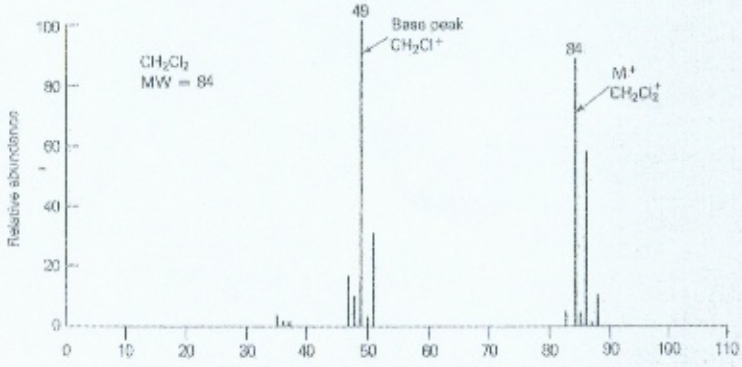



Fig. 2

3. From the proton spectrum given in Fig. 3, which is a commonly used pain-killer; its empirical formula is $C_{10}H_{13}NO_2$. Identify the structure and explain. (10%)

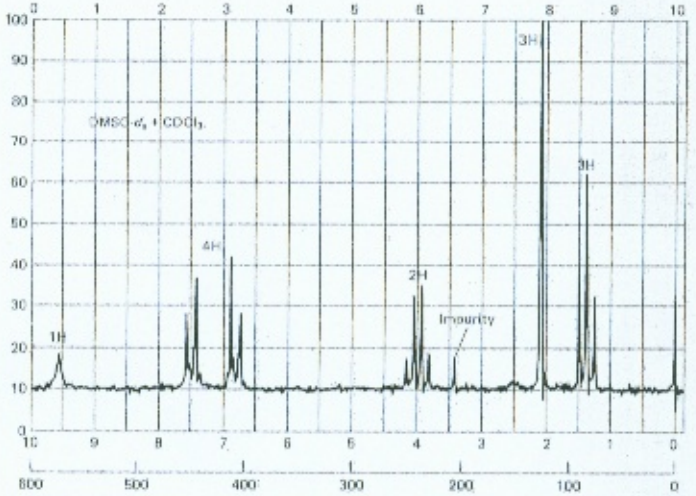
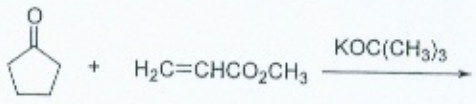
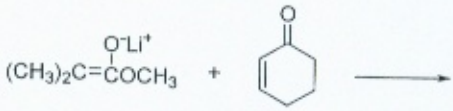
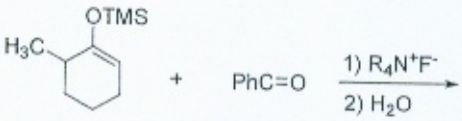



Fig. 3

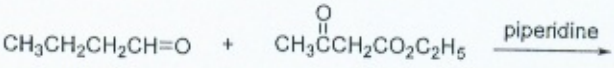
I. Give the major product(s) of the following reactions (50%)

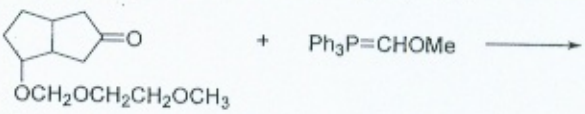
1. 

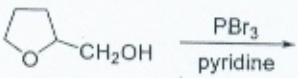

2. 

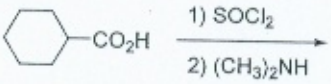

3. 

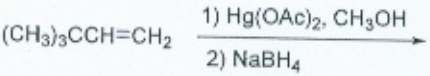

4. 

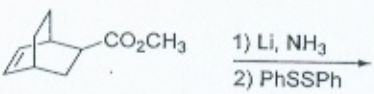

5. 

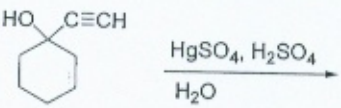

6. 

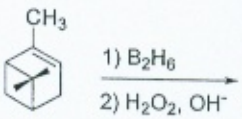

7. 

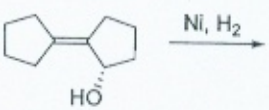

8. 

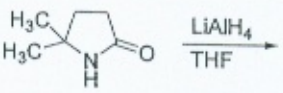

9. 

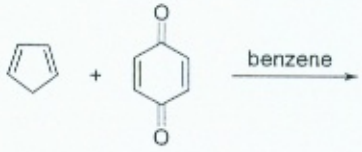

10. 

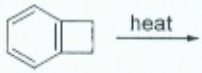

11. 

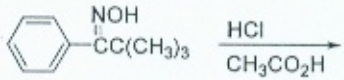

12. 

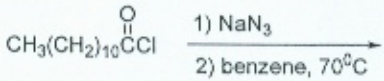

13. 

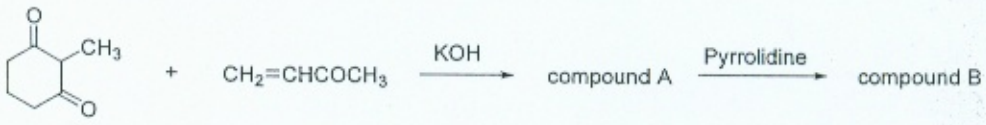

14. 

15. 

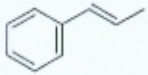
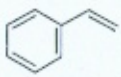

16. 


17. 


18. 


19. 


II. a) Propose a synthesis of 2,4,6-trinitrobenzoic acid from benzene.

b) Propose a synthesis of  from  . (16%)

III. How would you use $^{1}H$ NMR to distinguish between the following pairs of isomers? (6%)

$H_2C{=}C(CH_3)\overset{O}{\overset{\|}{C}}CH_3$ and $CH_3CH{=}CH\overset{O}{\overset{\|}{C}}CH_3$

IV. How many absorptions would you expect to observe in the $^{13}C$ spectra of the following compounds? (4%)

a. 3-methyl-1-pentyne　　b. *tert*-butylcyclohexane

V. Why the tertiary carbocation is more stable than the primary carbocation? (6%)

VI. Please explain "HOMO", "torsional strain", "chemical shift" and "keto-enol tautomerism" How to use the organic chemistry in your life? (10%)

VII. Give an example for each of the following name reactions: (8%)

a. Hofmann elimination reaction　　b. Fridel-Crafts acylation