

八十四學年度 輻射生物研究所 組碩士班研究生入學考試

科目 有機化學 科號 3403 共 4 頁第 1 頁 *請在試卷【答案卷】內作答

1. Choose the answer which best completes the indicated statement. (10%)
 - a) Enol forms of β -diketones are stabilized by _____.
 - (A) dimer formation. (B) charge dispersal. (C) the β -effect.
 - (D) hydrogen bonding.
 - b) Phenol is increased in acidity by _____.
 - (A) increasing its concentration. (B) reaction with methanol.
 - (C) dissolution in pyridine. (D) nitro substitution in the para position.
 - c) Aniline is more basic than _____.
 - (A) p-methylaniline. (B) N-methylaniline. (C) diethylamine.
 - (D) pyrrol.
 - d) Tertiary alcohols are _____.
 - (A) readily deoxygenated to the saturated hydrocarbon.
 - (B) more acidic than secondary alcohols.
 - (C) oxidized under basic conditions.
 - (D) readily dehydrated under acidic conditions.
 - e) The cyclooctatetraenyl dianion is _____.
 - (A) aromatic. (B) non-planar. (C) stable only in methanol solution.
 - (D) non-absorbing in the UV region.

2. Explain briefly the following chemical observations. Properly annotated diagrams or structures should be used. (15%)
 - a) Acetylacetone, as a pure liquid, exists principally in the enol form.
 - b) Trichloroacetic acid is a stronger acid than acetic acid.
 - c) The compound 6,6'-dibromobiphenyl-2,2'-dicarboxylic acid is obtainable in optically active forms in spite of the fact that the molecule contains no chiral atom.
 - d) Pyrrole is insoluble in water, but its saturated analog, pyrrolidine, is completely miscible with water.
 - e) The tertiary amine $(\text{CH}_3)_3\text{N}$ boils so much lower than its primary isomer $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$.

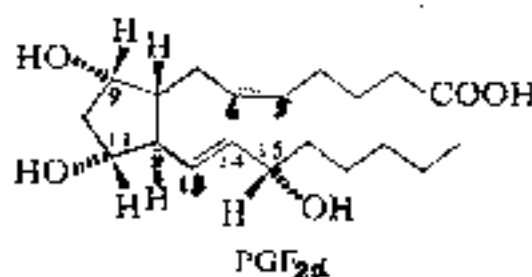
3. Reduction of D-fructose with NaBH_4 gives a mixture of D-glucitol and D-mannitol. What does this result prove about the configurations of D-fructose, D-mannose, and D-glucose? (4%)

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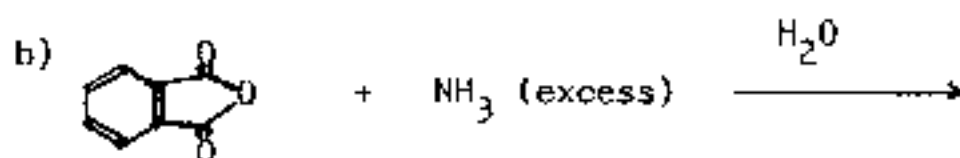
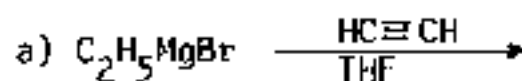
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4. Oxidation of either D-erythrose or D-threose with nitric acid gives tartaric acid. In one case, the tartaric acid is optically active; in the other, it is optically inactive. How can these facts be used to assign stereochemical structures to erythrose and threose? (4%)

5. Consider the structure of PGF_{2α}. (8%)

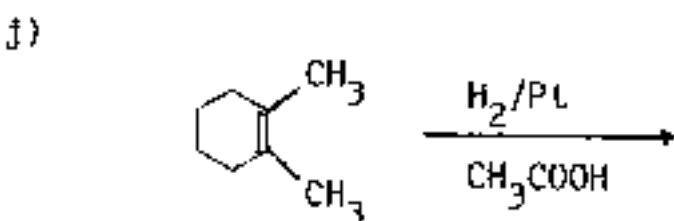
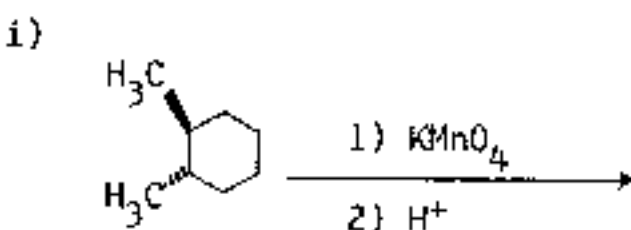
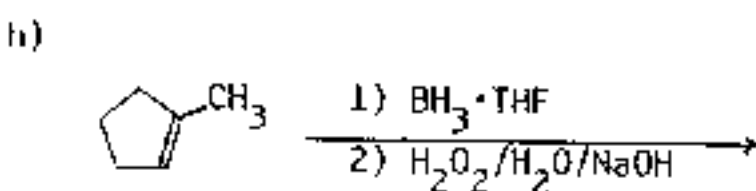
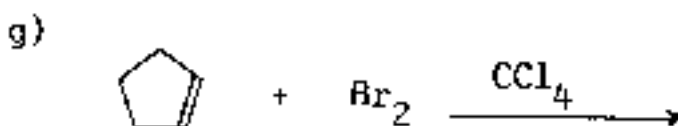
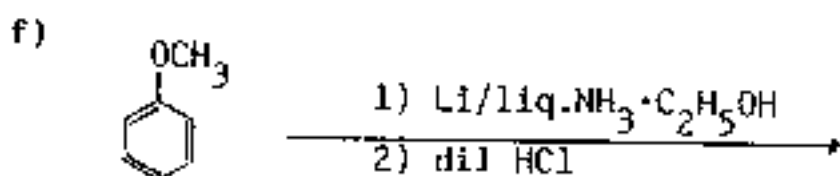
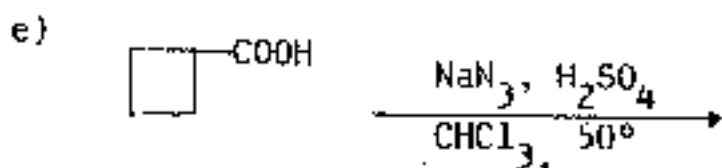
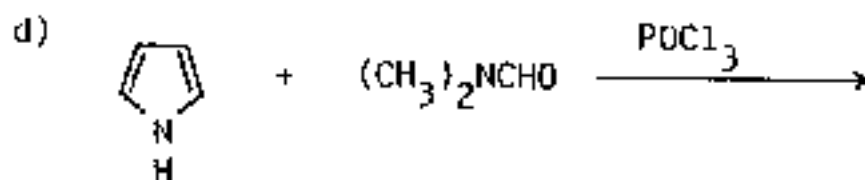
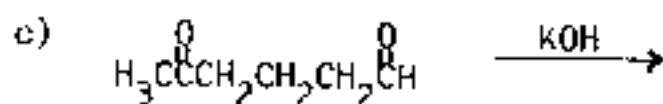


- How many chiral centers are present?
 - What is the configuration (R or S) of each?
 - What is the configuration of the double bonds (Z or E) in the two side chains?
 - Are the two side chains cis or trans to one another?
 - What each of the words (PG, F, α, and ~~α~~) means?
6. A compound, C₃H₆O, has no bands in the infrared region around 3500 or 1720 cm⁻¹. What structures can be eliminated by these data? Suggest a possible structure, and tell how you could determine whether it is correct. (9%)
7. How could you use simple chemical tests to distinguish between the following pairs of compounds. Describe exactly what you would observe in each case. (8%)
- styrene and cinnamic acid
 - formic acid and acetaldehyde
 - 2-pentanol and 3-pentanol
 - triethylamine and dipropylamine
8. Predict the products of the following reactions. Specify the stereochemistry clearly if necessary. (24%)



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9. Optically active 2-bromobutane undergoes racemization on treatment with a solution of KBr. Give a mechanism for this racemization. (8%)
10. A compound of formula $\text{C}_{11}\text{H}_{16}\text{N}_2$ gives the IR, ^1H NMR, and ^{13}C NMR spectra shown below. The proton NMR peak at $\delta 1.57$ disappears on shaking with D_2O . Propose a structure for this compound, and show how your structure accounts for the observed absorptions. (10%)

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