

Time: 2 1/2 Hours.

Chemistry 212

June 24, 1998

Final ExaminationH. SleimanName:Major:Student Number:

I. (25 pts)

a. Compound **A** has the following spectral features:

Mass Spectrum	IR Spectrum	<sup>1</sup> H NMR Spectrum
m/e 150 (30%)	3600 cm <sup>-1</sup> (broad)	δ 1.2 (doublet, 6H)
135 (100%)	2850-3100 (strong)	2.3 (singlet, 3H)
other small peaks	other peaks	3.2 (septet, 1H)
		4.7 (broad singlet, 1H)
		6.8 (singlet, 1H)
		6.9 (doublet, 1H)
		7.2 (doublet, 1H)

Deduce the structure of **A**.

- b. Compound **B** (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) is soluble in dilute NaOH and dilute NaHCO<sub>3</sub>. When treated with bromine, **B** is converted to C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>Br<sub>2</sub> (**C**). Compound **B** is converted into C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> (**D**) by treatment with hydrogen over a catalyst. Compound **D** loses a molecule of water when heated, and the acid anhydride thus produced reacts with benzene in the presence of aluminum chloride to give C<sub>10</sub>H<sub>10</sub>O<sub>3</sub> (**E**). **E** is soluble in base, reacts with phenyl hydrazine, is converted to benzoic acid by vigorous oxidation and exhibits the following <sup>1</sup>H NMR spectrum: δ 2.8 (triplet, 2H); 3.3 (triplet, 2H); 7.2-7.6 (multiplet, 3H); 8.0 (multiplet, 2H); 11.7 (singlet, 1H).

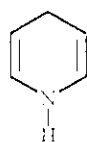
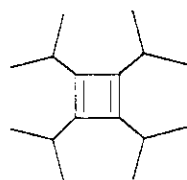
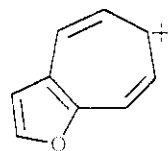
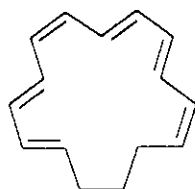
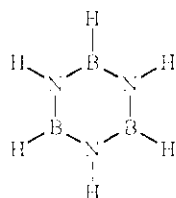
Deduce the structures of **B** through **E**

c. Compound F ( $C_4H_7Cl_3$ ) has the following  $^1H$  NMR spectrum:

- $\delta$  0.9, triplet, 3H
- 1.7, multiplet, 2H
- 4.3, multiplet, 1H
- 5.8, doublet, 1H

Deduce the structure of F.

II. Indicate if the following molecules are aromatic, non-aromatic, or antiaromatic.  
(15 pts) No explanation needed



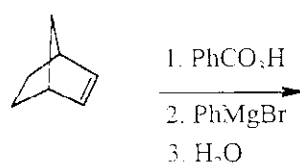
III. Draw the  $\pi$ -molecular orbitals of cyclobutadiene, and arrange them in increasing energy.  
(8 pts)

IV. Give the products of the following reactions with stereochemistry, when applicable. If no reaction takes place, write "no reaction"

1.

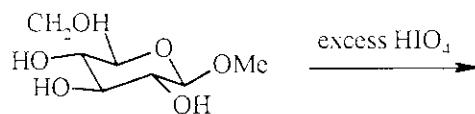


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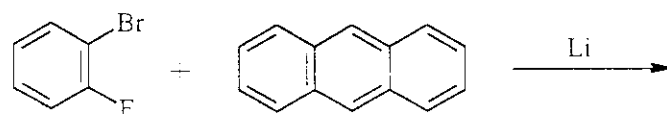


show stereochemistry in product

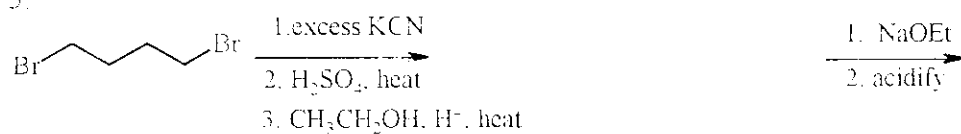
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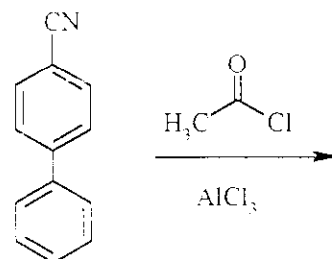
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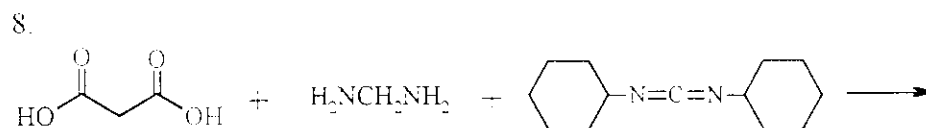
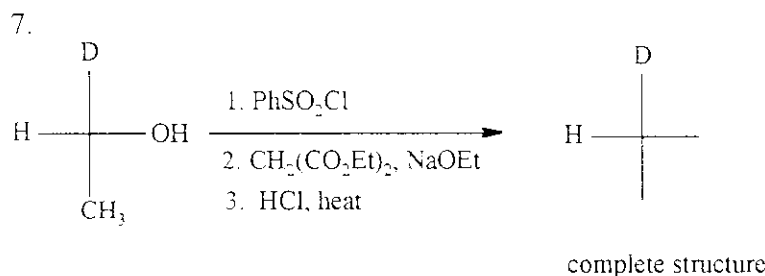


5.



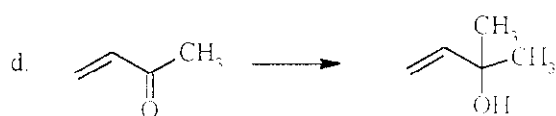
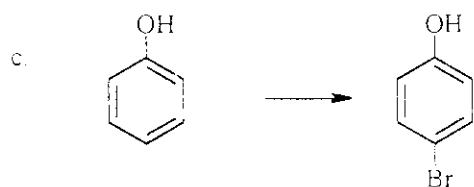
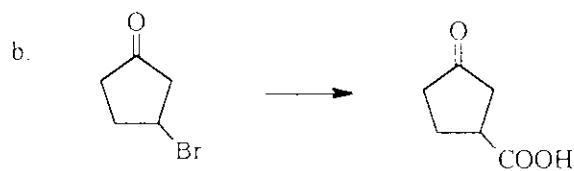
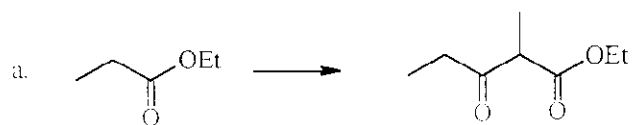
6.





V. For each of the following, circle the correct answer. Only one answer is correct.  
 (32pts) No penalty for wrong answers.

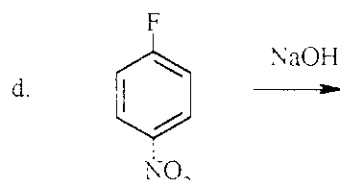
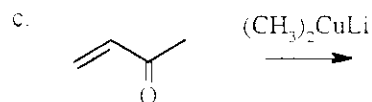
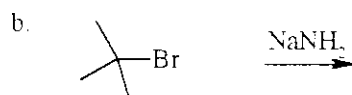
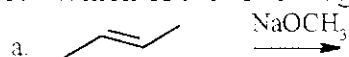
1. Which of the following transformations requires the use of a protecting group?



2. Circle the incorrect statement:

- The Williamson synthesis is a reaction used to make ethers
- The Tollen's reaction is used to make carboxylic acids from aldehydes
- The Canizzaro reaction is used to make alcohols and carboxylic acids from aldehydes
- The haloform reaction is used to make  $\alpha$ -haloacids
- The Reimer-Teimann reaction is used to make o-hydroxybenzaldehydes

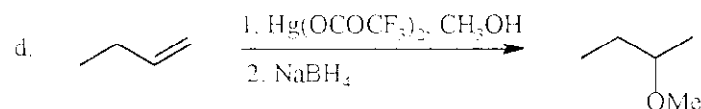
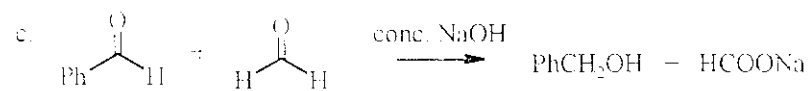
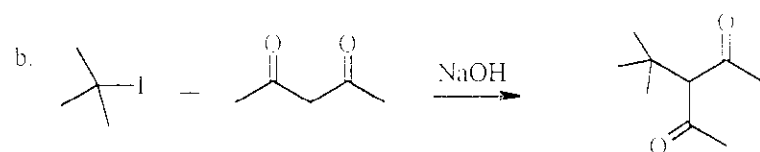
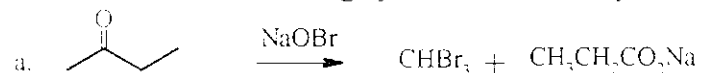
3. Which of the following reactions does not proceed under normal conditions?



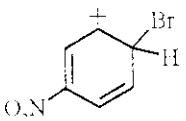
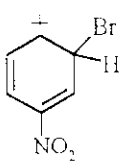
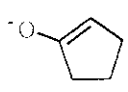
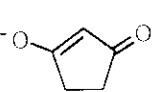
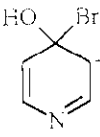
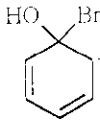


4. Which feature may be deduced from the UV/VIS spectrum of an organic compound?

- The presence of halides
- The vibrational states of a molecule
- The presence of conjugated double bonds
- The structure of the crystal
- The rotational states of a molecule

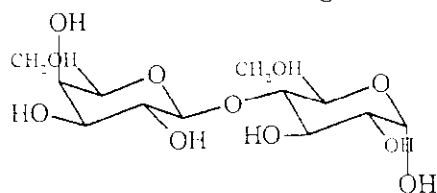
5. Which of the following syntheses is unlikely to be correct?



6. Circle the correct statement:

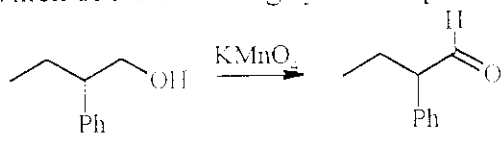
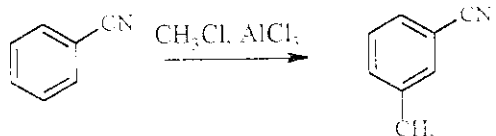
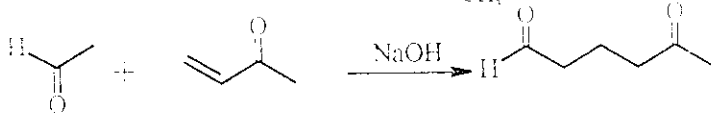
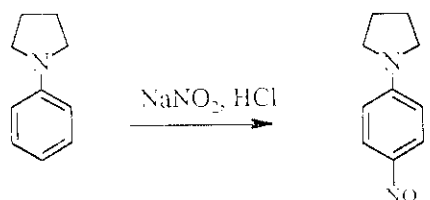
- a.  is more stable than 
- b.  is more stable than 
- c.  is more stable than 
- d.  is more stable than 

7. Lactose has the following structure; circle the incorrect statement:



- a. Lactose is 4-O-( $\beta$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside  
 b. Lactose reduces Tollen's reagent  
 c. Lactose reacts with  $\text{Br}_2/\text{H}_2\text{O}$   
 d. Lactose is hydrolyzed by  $\text{H}^+/\text{H}_2\text{O}$  into D-glucose and D-galactose

8. Which of the following syntheses proceeds with a reasonable yield?

- a. 
- b. 
- c. 
- d. 

- VI. (12 pts) Aldohexose **A** is reduced by  $\text{NaBH}_4$  into an optically inactive alditol **B**. Ruff degradation of **A** gives aldopentose **C**, which is oxidized by nitric acid into an optically active aldaric acid **D**. Give the name and structure of compounds **A** through **D**.

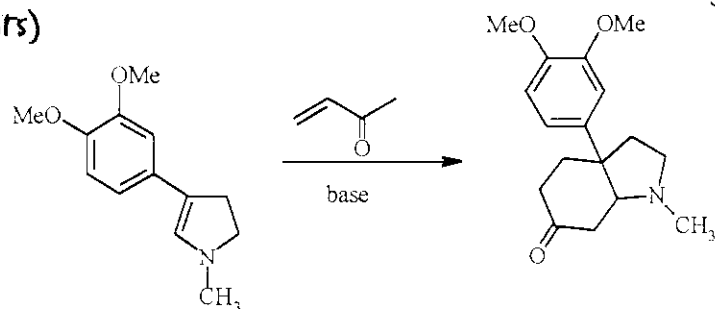
- VII. (12 pts) Oxytocin is a nonapeptide hormone secreted by the pituitary gland. Its function is to stimulate uterine contraction, and lactation, in childbirth. Its sequence was determined from the following evidence:

- Oxytocin is a cyclic compound containing a disulfide bridge between two cysteine residues
- When the disulfide bridge is reduced, oxytocin has the constitution: Asn, Cys<sub>2</sub>, Gln, Gly, Ile, Leu, Pro, Tyr
- Partial hydrolysis of reduced oxytocin yields seven fragments:
 

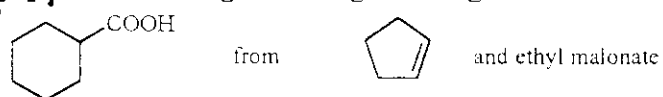
H-Asn-Cys-OH	H-Ile-Gln-OH
H-Cys-Tyr-OH	H-Leu-Gly-OH
H-Tyr-Ile-Gln-OH	H-Gln-Asn-Cys-OH
H-Cys-Pro-Leu-OH	
- Gly was shown to be the C-terminal residue

On the basis of this evidence, what is the structure of reduced oxytocin? (use amino acid symbols). What is the full chemical structure of oxytocin itself?

VIII. Write a reasonable mechanism for the following transformation:  
(12 pts)



IX. Provide a synthesis for the following from the indicated starting materials and any needed organic/inorganic reagents:  
(12 pts)



BONUS QUESTION (no partial credit; work only if you have a full synthesis)

