

UNIVERSITY OF TORONTO  
FACULTY OF APPLIED SCIENCE AND ENGINEERING  
CHE 391s Organic Chemistry and Biochemistry  
Final Exam - Tuesday April 17, 2001  
EXAMINER: Prof. E.A. Edwards

Answer all questions in the spaces provided. (14<sup>+</sup> pages; 19 questions)

Name \_\_\_\_\_ Student Number: \_\_\_\_\_

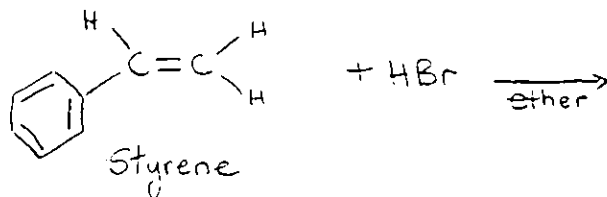
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Minutes

Questions:

1. Predict the major (and significant minor) products of the reactions below (briefly justify your answer and name reaction type or mechanism; include stereochemistry where appropriate):

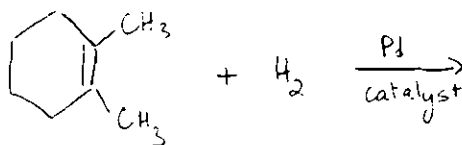
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a)



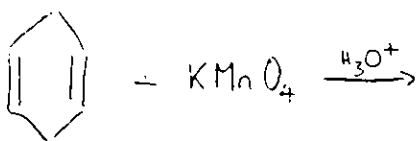
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b)

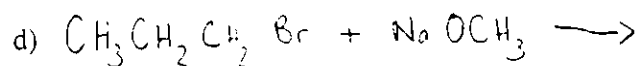


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c)



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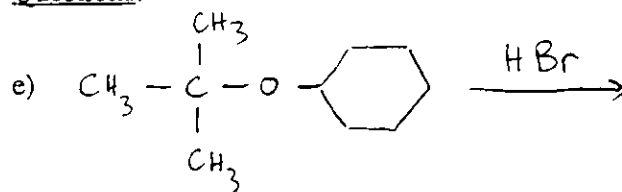


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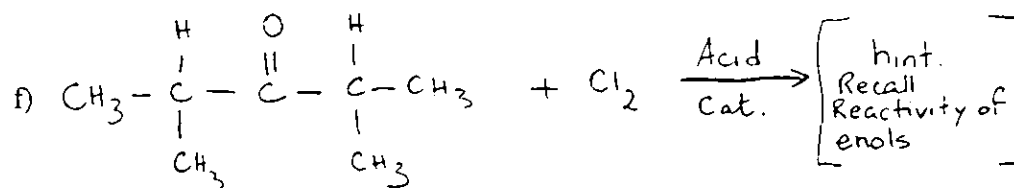
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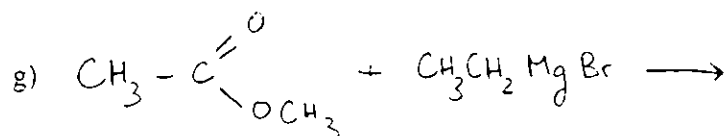
Questions:



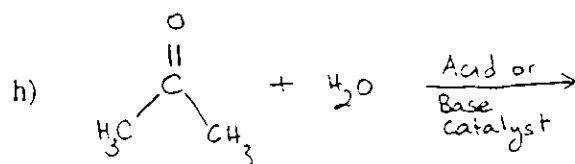
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2



2



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Questions:

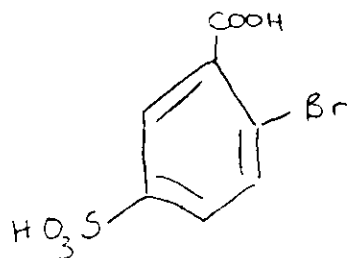
- 2      2. Rank the following compounds in order of increasing acidity. ? Justify your answer.
- a)  $\text{CH}_3\text{CH}_2\text{COOH}$    b)  $\text{BrCH}_2\text{CH}_2\text{COOH}$    c)  $\text{BrCH}_2\text{COOH}$
- 4      3. a) How would you prepare *p*-aminotoluene from *p*-nitrotoluene?
- 5      b) This reaction does not go to completion. How would you separate the amine from the un-reacted nitro compound? (write out each step in your separation scheme)

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Questions:

- 3      4. c) Rank these compounds in order of increasing basicity. Justify your answer.  
  
          *p*-chloroaniline, aniline, cyclohexylamine, phenol
- 6      5. How would you synthesize the following substituted benzene from benzene (Hint: you need 4 steps)

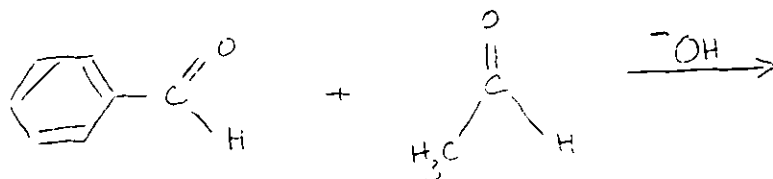


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Questions:

- 2      6. The  $pK_a$ s of  $\text{NH}_4^+$  and  $\text{CH}_3\text{NH}_3^+$  are 9.30 and 10.64, respectively. Which is the stronger base,  $\text{NH}_3$  or  $\text{CH}_3\text{NH}_2$ ? Why?
- 3      7. Rank the following compounds in order of decreasing boiling points
- a.  $\text{CH}_3\text{CH}_2\text{OH}$
  - b.  $\text{CH}_3\text{CH}_2\text{COOH}$
  - c.  $\text{CH}_3\text{CH}_2\text{CH}_3$
  - d.  $\text{CH}_3\text{CH}_2\text{NH}_2$
- 6      8. Write the reaction mechanism for the following reaction: (show all steps). Recall - this was on your last quiz.....

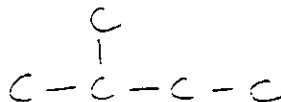


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Questions:

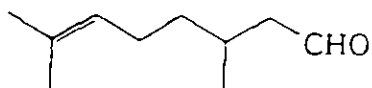
9. The five-carbon unit with a four carbon chain and a one carbon branch at C2 is called an isoprene unit. Compounds with a single isoprene unit (C<sub>5</sub>) are relatively rare in nature, but compounds with two such units (C<sub>10</sub>), called monoterpenes, are common.



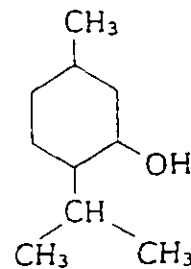
Isoprene unit

2

- a) Mark off the isoprene units in citronellal and menthol. (i.e., draw a line to divide the molecules into isoprene units)



citronellal



menthol

2

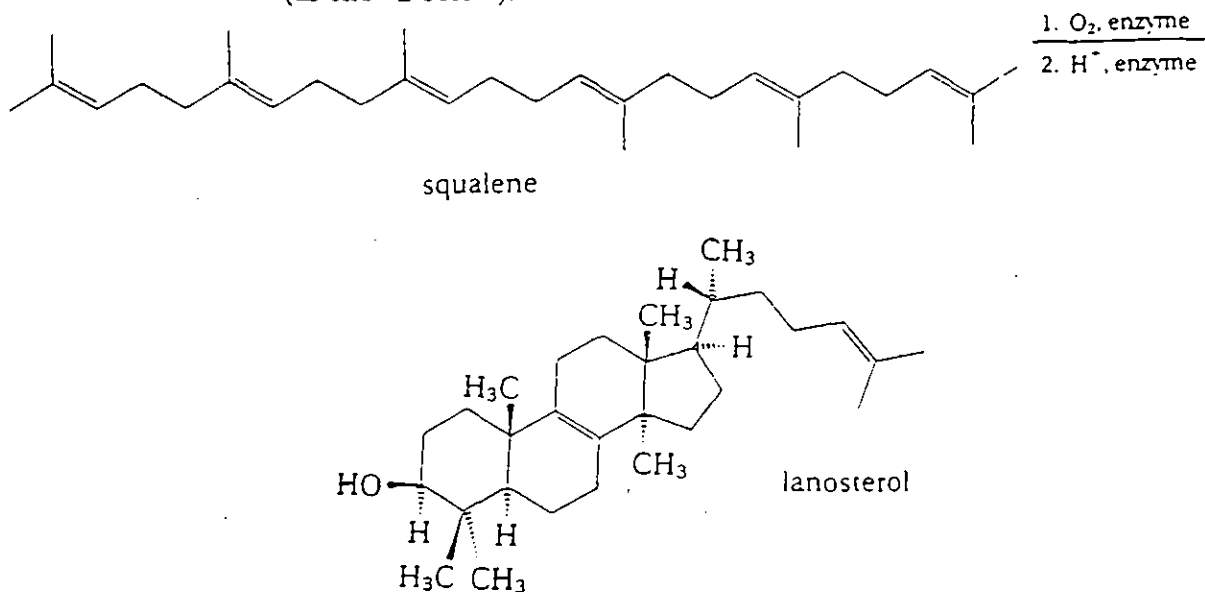
- b) What is the principal functional group (PFG) in each of these molecules?

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Questions:

- c) Steroids constitute a major class of lipids. Through a truly remarkable enzymatic reaction sequence, the acyclic triterpene squalene is converted stereospecifically to the tetracyclic steroid lanosterol, from which other steroids are subsequently synthesized (as shown below).



- 2      b) How many carbon atoms are present in squalene? In lanosterol?
- 3      c) What is the configuration (Z, E) of each of the double bonds in squalene?
- 4      d) How many stereogenic centers are present in squalene? In lanosterol?
- 2      e) Name a steroid hormone.

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Questions:

10. Consider D(+)-galactose (refer to attached table for structure).

- |   |  |
|---|--|
| 2 | a) What do the terms "D" and "(+)" mean preceding the name of the sugar? |
| 2 | b) How many stereogenic centres does D(+)-galactose have?                |
| 2 | c) How many isomers of D(+)-galactose exist?                             |
| 4 | d) Draw the enantiomer of D(+)-galactose.                                |
| 4 | e) How many diastereoisomers of D(+)-galactose exist.                    |



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Questions:

11. The British carbohydrate chemist, W. N. Haworth (Nobel prize, 1937) introduced a useful way of representing the cyclic forms of sugars.

5

a) Draw the Haworth projection of the pyranose form of D(+)-mannose. Only draw the  $\alpha$ -anomer. (use an arrow to point to the anomeric carbon)

3

b) D-Erythrose cannot exist in pyranose forms, but furanose cyclic forms are possible. Explain why this is.

5

c) D-Mannitol, which occurs naturally in olives, onions, and mushrooms, can be made by  $\text{NaBH}_4$  reduction of mannose. Draw its structure using a Fischer projection.

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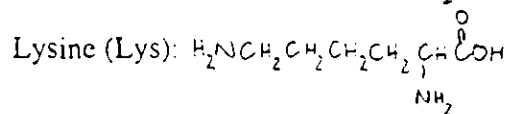
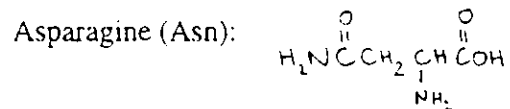
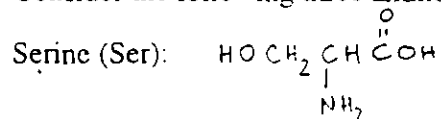
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Questions:

12. Cellulose is the raw material for several commercially important derivatives.

- 2 a) How many free hydroxyl groups are present on each glucose unit in cellulose?
- 4 b) These hydroxyl groups can be modified by the usual reagents that react with alcohols. What reagent would you suggest to produce cellulose acetate?

13. Consider the following three amino acids:



- 3 a) Classify these three amino acids as neutral, polar, acidic or basic.
- 6 b) Draw the tripeptide Ser-Asn-Lys as it would be found at pH 7.
- 3 c) What would the overall charge of this molecule be at pH=1?

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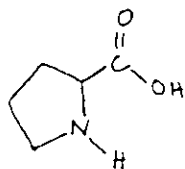
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Questions:

- 8      14. Fibrous proteins including keratins, collagens, and silks (for example skin, hair, feathers, claws, and nails, tendons, cocoons) have rigid shapes and are not water soluble. Globular proteins such as enzymes, hormones, transport proteins and storage proteins are more spherical and tend to be water soluble.

How do you think the primary, secondary and tertiary structures of these two general classes of proteins differ to account for these differences in physical properties?

- 3      15. How do you account for the fact that proline is never encountered in a protein  $\alpha$ -helix?



proline

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Questions:

16. Styrene (shown in question 1(a)) is easily polymerized by benzoyl peroxide, and the product, polystyrene, has a molecular weight in the range of 1 to 3 million g/mole. Polystyrene is a thermoplastic polymer.
- 4 a. Draw three repeat units of polystyrene.
- 3 b) How many monomers would your typical polystyrene molecule contain?
- 3 c) What is meant by a thermoplastic polymer?
- 3 c) Polystyrene can be modified in various ways. For example, it can be made more rigid through cross-linking by including small amounts of *p*-divinylbenzene with the monomer. Show how *p*-divinylbenzene could act as a cross-linking agent.

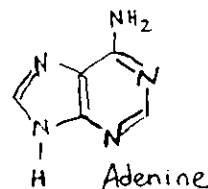
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Questions:

6

17. a) What are the 3 components that form a nucleotide of DNA? Identify these components by drawing the nucleotide called 2'-deoxyadenosine monophosphate (abbreviated dAMP), where the base is adenine (drawn below).



2

- b. What does the 2' refer to?

4

- c) Where and how are nucleotides linked together to form a polymer ?

5

- d) Nucleotides are not only found in DNA and RNA. ATP (adenosine triphosphate) is the energy currency of a cell. ATP contains two phosphoric anhydride bonds, and considerable energy is released when ATP is hydrolyzed to ADP and further to AMP. Although we did not formally study the structure of this molecule, you should be able to deduce its structure from the information above. Draw a molecule of ATP.

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Questions:

- 4      18. The human genome contains 3 billion base pairs. Estimate the length (in cm) of DNA in a human cell. State your assumptions.
- 10      19. Which of the following statements are true and which are false? Correct false statements.
- a. All amino acids are S-amino acids.
  - b. DNA polymerase catalyzes replication of DNA in the 3' to 5' direction
  - c. A disulphide bond can be important for the tertiary and quaternary structures of a protein
  - d. mRNA is a very unstable molecule
  - e. Oils contain a much higher percentage of unsaturated fatty acids than do fats.
  - f. The quaternary structure of proteins includes 4 sub-units.
  - g. A  $\beta$ -pleated sheet is a folded tablecloth.
  - h. The fluid mosaic model refers to the tiles on the bottom of a swimming pool

The END

Figure 14.3

# Configurations of D aldoses

