CHEM 163/263 SAMPLE FINAL Dr. John C. Vederas

I. Structure and Nomenclature - 91 Points -

A. Draw structures for which names are given, or name the given structures by any correct (systematic or common) nomenclature. Be sure to give cis or trans (or if appropriate Z or E) or R or S assignment to the isomer where indicated by asterisks (***). (4 points each - 60 points total)

1. pyridine (commonly used as base or solvent)

2. ethylene glycol (constituent of anti-freeze)

3. benzyl vinyl ether

4. urea

5. valeryl chloride

6. D-glucose (open chain form)

(use part structure below in your drawing to assist grading) if you make an error, redraw part structure

**** 7. (Assign R or S configuration)

(3R),(4E)-3-chloro-4-hexenoyl chloride

8. calcium propionate (a food preservative)

**** **9.** pheromone from moths

cis-7-dodecenyl acetate

or cis-7-dodecenyl ethanoate

**** 10. an addictive street drug

(2R)-1-phenyl-2-aminopropane (amphetamine)

**** 11. substance in hooves of South African antelopes used for social recognition

cis-5-undecen-2-one

12. a pheromone that induces interspecies mating of male cotton bollworms with female tobacco worms thereby killing both (a C16 compound)

cis-11-hexadecen-1-ol

13. biological precursor for inflammatory substances (a C20 compound)

all cis (or all Z) 5,8,11,14-eicosatetraenoic acid

or arachidonic acid

14. induces flowering in fruit trees

2,3,5-triiodobenzoic acid

****15. (R)-1-cyclopentyl-2-(N-methylamino)propane a nasal decongestant

(use part structure to assist grading - if you make an error redraw part structure)

B. Determine whether the following pairs of structures are identical (i.e. different pictures of the same molecule), structural isomers, diastereomers, or enantiomers. (2 points each - 8 pts total).

1.

2.

3.

4.

C. Lactose, also known as milk sugar, comprises about 7 % of human milk. Examine its structure and answer the questions which follow. (10 pts + 6 pts = 16 pts total)

- 1. The number of carbons in lactose is: 12
- 2. The number of hydrogens in lactose is: 22
- **3.** The number of stereogenic centres in lactose is: **10**
- 4. The total number of acetal and hemiacetal carbons in lactose is: 2
- 5. The number of non-hydrogen equatorial substituents (bonds) in lactose is: 9
- 3. Indicate whether the following statements are true (T) or false (F). No penalty for guessing.

- a. Lactose is a reducing sugar. True
- b. The parent sugar units of lactose are aldopentoses False
- c. At least one of the sugar units of lactose is a beta-glucopyranoside True
- d. Lactose is composed only of L-sugars False
- e. Lactose could be made by coupling of two identical monosaccharides False
- g. The lactose structure shown is easily isomerized in water True

II. Physical Properties and Definitions - 62 Points

A. Examine the compounds **1-15** in the group below and answer the questions which follow. Be sure to write your answer clearly. (**13 points - 8 pts + 5 pts**)

- 1. In the group of compounds 1-5 only, the most acidic compound is number 4
- 2. In the group of compounds 6-10 only, the most acidic compound is number 8
- 3. In the group of compounds 11-15 only, the most volatile (lowest boiling point) is number 12
- 4. In the entire group 1-15 inclusive, the most basic compound is number 3
- **5.** Indicate whether the following statements are true (**T**) or false (**F**)

(1 pt each - 5 pts total)

- a. Compounds 3, 4, 8, 11, and 15 are miscible (completely soluble) with water True
- b. Compounds 1, 2, 5, 12, and 13 are not miscible with water True
- c. Compound 14 is soluble in 1N NaOH solution True
- d. Molecules of compound 4 can hydrogen bond to each other True
- e. Compound 6 is a food additive used in salt and vinegar potato chips False
- **B.** A number of terms are given below with an identifying letter directly underneath. Make the best match of these terms with the short statements which follow by putting the correct letter on the line provided after the statement. Use each letter no more than once. (24 Points total 2 pts each)

	Meso Compounds	Dyes	Racemate	Elimination Reactions	
A	В	C	D	E	F

E2 Reactions	Atomic Numbers	Stereospecific Reaction	Alkaloid	Resonance Forms	Tautomers
G	H	I	J	K	L

				л
Undrida		IHnol I	Wittin	

Anion	Cellulose	Vitamin C	Oxidations		Reaction
M	N	P	Q	R	S

Estrogens	Grignard Reactions
T	U

- 1. Polysaccharide N
- 2. Diels Alder I
- 3. Ylides S
- 4. Reductions M
- 5. Carbocation Intermediates A
- **6.** Structural Isomers L
- 7. Nitrogen Compounds J
- **8.** Enantiomer Mixture **D**
- **9.** Azo Compounds **C**
- 10. Alkyl Anions U
- 11. Walden Inversions F
- 12. Ozonolyses Q

C. It would be predicted that one of the two phenolate anions shown below would form more readily and be more stable. Circle the more stable structure (1 pt) and draw the extra resonance form which accounts for this behaviour by completing the partially drawn structure on the right. (4 points total)

D. Seven compounds whose properties and importance were discussed in class are shown below. Identify each compound by carefully PRINTING its name on the line provided below it. Illegible answers will be marked as incorrect. (21 points total - 3 pts each)

No Sample Questions or Answers available here

III. Reactions - 84 Points

A. Show the structure of the major organic product of each of the following reactions. Show stereochemistry where indicated by asterisks (***). (30 Points total - 3 pts each)

1.

2.

$$\begin{array}{ccc}
& & \frac{H_2SO_4}{SO_3} & & & \\
& & & & \\
\end{array}$$

*** **4.**

5.

6.

7.

***8.

9.

$$\begin{array}{c|c}
\text{COOH} & \downarrow \text{O} & \downarrow \\
\text{NH}_2 & \downarrow \text{COId}
\end{array}$$

B. A number of reagents are given below with an identifying letter directly underneath. Examine the transformations which follow and print carefully the correct letter for the best reagent on the line provided after the reaction. You may need to use a particular reagent letter more than once, but put only one letter per line. (27 pts)

Br2 and light	Br2 in dark		LiAlH4 then water	CrO3
A	В	C	D	E

water and HCl	water and NaOH	Zn/Hg in HCl	Mg in dry ether	KMnO4
F	\mathbf{G}	H	\mathbf{J}	K

lithium diisopropylamide	CH3COCl, AlCl3	O3 then Zn	H2 and Pd	H2SO4
L	M	N	P	Q

NaOCH3,	HCl,	CH3CHO,	СН3СН2ОН	NaNO2,
CH3OH	CH3OH	base		HCl, H2O
R	S	T	U	X

1.

2.

$$\stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\longrightarrow}$$

$$\overset{\circ}{\bigcirc} \overset{\mathsf{T}}{\longrightarrow} \overset{\circ}{\bigcirc} \overset{\circ}{\bigcirc}$$

4.

5.

6.

7.

8.

$$\bigcirc \qquad \stackrel{\mathsf{N}}{\longrightarrow} \qquad \bigcirc_{\mathsf{o}}^{\mathsf{o}}$$

C. Warfarin is a commercial rat poison which works by preventing blood clotting through interference with Vitamin K metabolism, thereby causing the animals to bleed to death. The synthesis of warfarin from a well known drug is shown below. The last step involves base-catalyzed (pyridine) Michael condensation of an alpha, beta-unsaturated ketone. Put the correct structure of this ketone in the space under number 5 below. Print the correct letter for the best reagent on the line next to the number of its reaction given below the scheme. Be sure that you put the letters in the correct location. (15 points total - 3 pts each)

Br2 and light	Br2 in dark	CO ₂		(CH3CO)2O and base
A	В	C	D	E

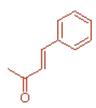
Cr3O	water and NaOH	Zn/Hg in HCl	Mg in dry ether	KMnO4
F	G	H	J	K

lithium	· · · · · · · · · · · · · · · · · · ·	B2H6 then	H ₂ and Pd	H2SO4
diisopropylamide	AIC13	H2O2		(conc)
L	M	N	P	Q

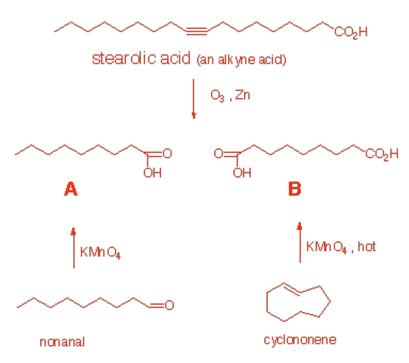
NaOCH3,	HCl,	СН3СНО,	CHaCHaOH	NaNO2,
СН3ОН	СН3ОН	base	CH3CH2OH	HCl, H2O
R	S	T	U	X

- 1. **G**
- 2. **S**
- 3. E

5.



D. Treatment of stearolic acid (C18H32O2) with ozone and then zinc gives two compounds: compound **A** (C9H18O2) and compound **B** (C9H16O4). Oxidation of nonanal with H2CrO4 (or with KMnO4) also produces **A**. Heating of cyclononene with hot KMnO4 gives **B**. What are the structures of stearolic acid, compound **A**, and compound **B**? (**4 pts each - 12 pts total**)



IV. Synthesis - 23 Points Total

A. Devise a synthesis of 5-methyl-5-propylbarbituric acid (a sleep-inducing barbituate) from carisoprodol, a powerful muscle relaxant. (**12 points**)

B. Pantothenic acid (Vitamin B3) is an essential nutrient. Part of its chemical synthesis is outlined below. Supply the missing reagents and products and answer the questions below the scheme. (**18 points**)

Hint: Examine each structure in terms of negative and positive sites and try to attach the missing atoms necessary for the products by using stable molecules with appropriate charge distribution.

Provide the structures of 1 through 4: (3 pts each - 12 points)

- a. What is the other produced in the spontaneous ring formation ? (2 pts) Water i.e. H2O
- **b.** Name all functional groups in the cyclic material as specifically as you can. (**2 pts**) Lactone (Cyclic Ester), Alcohol
- c. Name the functional group with the triply bonded nitrogen (2 pts) Cyano or Nitrile or Cyanide

V. Mechanism - 33 Points Total

Four mechanisms for the hydrolysis of an ester are depicted below. They may be reasonable or unreasonable; in some cases whether the mechanism is correct may depend on the reaction conditions. Examine the possibilities carefully and answer the questions which follow by placing the correct letters in the boxes. (18 pts)

$$\mathbf{B} \xrightarrow[]{\circ} \mathbb{C}$$

3 points each - Letter(s) of Answer(s):

- 1. The best mechanism for hydrolysis of a methyl ester at pH 10 would be: B
- 2. The best mechanism for hydrolysis of a methyl ester at pH 1 would be: C
- 3. The letter(s) of mechanism(s) which may be correct sometimes are (put E if all are incorrect): B and C

- **4.** The letter(s) of mechanism(s) which can never be correct are (put **E** if all are correct): **A** and **D**
- **5**. Hydrolysis of an ester at pH 1 is easily reversible by adjustment of water concentration (T or F): **True**
- **6.** Hydrolysis of an ester at pH 10 is easily reversible by adjustment of water concentration (T or F): False

A mechanism for an electrophilic aromatic substitution reaction is shown below, but it is missing charges and the arrows showing the movement of electrons. Put in the correct charges on the appropriate atoms and used curved arrows to indicate movement of electrons. (15 points)

Overall Reaction

Mechanism - fill in missing arrows and charges below