EID		<del></del>	Chemistry 320N 2nd Midterm Exam March 7, 2024	
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SIGNATURE	:			
	Please print the first three letters of your last name in the three boxes			

**Please Note:** Please take your time. You have three hours to take this exam. Please do not rush, we want you to show us everything you have learned this semester so far! Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

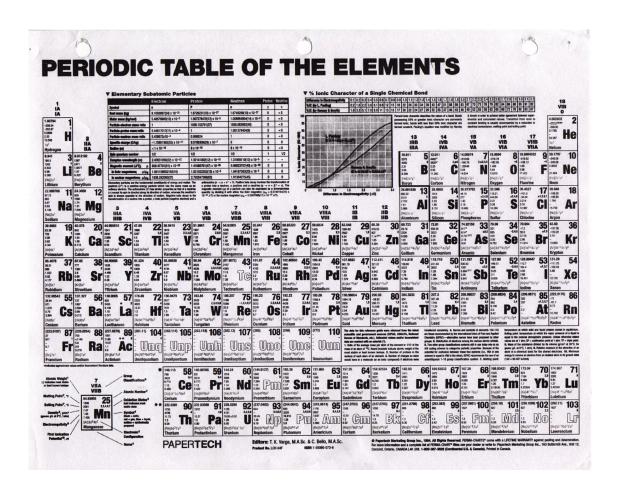
## Student Honor Code for the University of Texas at Austin

"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

## Elaboration

- 1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
- 2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
- 3. This code encompasses all of the academic and scholarly endeavors of the university community.

(Your signature)



Comp	ound	рK <sub>а</sub>
Hydrochloric acid	<u>H</u> -Cl	-7
Protonated alcohol	⊕ RCH <sub>2</sub> O <mark>H</mark> 2	-2
Hydronium ion	<u>H</u> ₃O <sup>⊕</sup>	-1.7
Carboxylic acids	O    R-CO- <u>H</u>	3-5
Thiols	RCH₂S <mark>H</mark>	8-9
Ammonium ion	<u>H</u> ₄N <sup>⊕</sup>	9.2
β <b>-Dicarbonyls</b>	O O       RC-C <u>H</u> 2·CR'	10
Primary ammonium	⊕ M <sub>3</sub> NCH <sub>2</sub> CH <sub>3</sub>	10.5
β-Ketoesters	O O       RC-C <mark>H<sub>2</sub></mark> ·COR'	11
β-Diesters	O O       ROC-C <u>H</u> 2-COR'	13
Water	HO <mark>H</mark>	15.7
Alcohols	RCH₂O <u>H</u>	15-19
Acid chlorides	RC <mark>H<sub>2</sub>-CCI</mark>	16
Aldehydes	RC <mark>H<sub>2</sub>-</mark> CH	18-20
Ketones	RC <mark>H<sub>2</sub>-CR'</mark>	18-20
Esters	O    RC <mark>H</mark> <sub>2</sub> -COR'	23-25
Terminal alkynes	RC≡C— <mark>H</mark>	25
LDA	$\underline{H}$ -N( $i$ -C $_3$ H $_7$ ) $_2$	40
Terminal alkenes	$R_2C = C - \underline{\underline{H}}$	44
Alkanes	CH <sub>3</sub> CH <sub>2</sub> - <u>H</u>	51

**1.** (5 pts) What is the most important question in organic chemistry?

**2.** (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular medical diagnostic technique of 1. 2. 2. 3. ( ) is based on the same principles as 4.

namely the flipping (i.e. 5.\_\_\_\_\_\_) of nuclear spins of H atoms by

6.\_\_\_\_\_ frequency irradiation when a patient is placed in a strong

7.\_\_\_\_\_\_ 8.\_\_\_\_\_. Magnetic field 9.\_\_\_\_\_

are used to gain 10,\_\_\_\_\_\_ information, and rotation of the

11. \_\_\_\_\_ around the center of the object gives imaging in an entire plane (i.e.

12. \_\_\_\_\_ inside patient). In an MRI image, you are looking at individual

that when 14.\_\_\_\_\_ make up the three-

dimensional image of 15. \_\_\_\_\_ amounts of 16. \_\_\_\_\_ atoms,

especially the 17.\_\_\_\_\_ atoms from 18.\_\_\_\_\_ and

19.\_\_\_\_\_, in the different 20.\_\_\_\_\_.

**3.** (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided. (No need to draw any arrows for this.)



**4.** (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

Α.

В.

**C**. In the box, draw the structure corresponding to the following IUPAC name.

(E)-N,N-diethyl-3-methylpent-2-enamide or (E)-N,N-diethyl-3-methyl-2-pentenamide

5. (12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile in the mechanisms we have seen. Note that these species might be proton acids or bases in certain situations, but we will ignore that for this problem.

5.1

O

H

Electrophile

Nucleophile

5.5  $\ddot{N}_{H_2}$ Calculate Supering Su

Electrophile

Nucleophile

Electrophile

Nucleophile

Nucleophile

5.10

5.11

5.9

© Electrophile

5.6

○ Electrophile
○ Nucleophile

5.3 LiAlH<sub>4</sub>

 Electrophile
 Nucleophile

H ⊕ H

H

Electrophile

**Nucleophile** 

5.4 :OH :DH :Nucleophile

5.12 HSolution H

NH<sub>2</sub>

Electrophile

Nucleophile

**6.** (6 pts) For each structure below, draw the other important contributing structure. You do not need to draw arrows anywhere, but you must include all lone pairs and formal charges.

H<sub>3</sub>C C CH<sub>3</sub>

⊕

H<sub>3</sub>C C CH<sub>3</sub>

⊕

H<sub>3</sub>C C CH<sub>3</sub>

⊕

H

CH<sub>2</sub>

H<sub>3</sub>C CH<sub>3</sub>

| C CH<sub>3</sub>
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| C

**7.** (16 pts) As described in class, the reactivity of carboxylic acid derivatives with nucleophiles is correlated with leaving group ability. We also pointed out that leaving group ability can be correlated with the  $pK_a$  of the protonated form of the leaving group anion. Here are a series of related alcohols with their  $pK_a$  values listed below each one.

A) (1 pt each) Rank the stabilities of each of the following anions from 1-4. Put a "1" under the most stable anion, and a "4" under the least stable anion (then a "2" and "3" as appropriate).

B) (1 pt each) Rank the following esters from 1-4 for reactivty with nucleophiles such as HO or an amine. Put a "1" under the most reactive with nucleophiles, and a "4" under the least reactive with nucleophiles (then a "2" and "3" as appropriate).

C) (2 pts each) Rank the following carboxylic acid derivatives from 1-4 for reactivty with nucleophiles such as water or an amine. Put a "1" under the most reactive with nucleophiles, and a "4" under the least reactive with nucleophiles (then a "2" and "3" as appropriate).

$$\bigvee_{O} \bigvee_{O} \bigvee_{O$$

**8.** (12 pts) Being good at identifying relationships between molecules is an important skill in Organic Chemistry. Fill in the circle to identify the stereochemical relationship between each pair of molecules. In the boxes provided, you need to write whether each chiral center is "R" or "S".

**9.** (14 pts) The following two intermediates are encountered in the reaction of LiAlH<sub>4</sub> with amides and esters, respectively. In each case, draw the appropriate arrows and only the next intermediate of the mechanism. No need to continue on with the mechanisms, we only want arrows on the structures we drew, and we only want you to draw the next intermediate in the mechanism. Remember to write all products of the step, and include all lone pairs and all formal charges. In the box over the arrow, indicate what type of step this is (add a proton, make a bond, etc.) HINT: These are not the last steps of the mechanisms, so writing "Aluminum Salts" is not appropriate, you need to indicate the structure of the Aluminum species produced in this step.

$$\begin{bmatrix} H & Li \\ | \Theta & H \\ | AI \\ | AI \\ | N-H \\ | Racemic & H & H \end{bmatrix}$$

$$\begin{bmatrix} H & Li \\ | \Theta & H \\ | O & H \\ | O & H \\ | Racemic & H & | AI \\ | Racemic & H & | AI \\ | Racemic & H & | AI \\ | Racemic & H & | Racemic & H & | Racemic & |$$

Pg 6 \_\_\_\_\_(35)

10. (35 pts) For this reaction, use arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).

Ester Hydrolysis

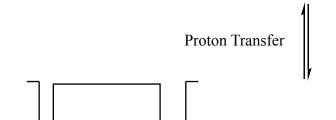
Signature	

Pg 7 \_\_\_\_(24)

11. (24 pts) For this reaction, use arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).</u>

Acid Chlorides Reacting with Amines

No need to draw arrows



Products of last step

12. (35 pts) For this reaction, use arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.). NOTE: For the chiral centers already on the starting material, you need to show them with WEDGES and DASHES, EVEN ON THE INTERMEDIATES).

Fischer Esterification

13. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. NOTE:

$$\begin{array}{c} \text{1)} & \text{H} \\ \text{O} \\ \text{CH}_{2}\text{CH}_{3} \\ \\ \text{MgBr} \\ \hline \\ \text{2)} & \text{HCl} \, / \, \text{H}_{2}\text{O} \\ \end{array}$$

$$Cl$$
  $2$   $NH_2$ 

13. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get full credit, you only need to write the major organic product for these. You do not have to worry about the other products.

$$\begin{array}{c|c}
O \\
\hline
NH & 1) LiAlH_4 \\
\hline
2) H_2O
\end{array}$$

$$O-CH_3$$

$$O \qquad 1) \qquad 2 \qquad MgBr$$

$$2) \quad HC1/H_2O$$



$$Cl \qquad 1) \qquad 2$$

$$2) \quad HCl/H2O$$

$$O \qquad \qquad NH_2 \longrightarrow PH = 4$$

**14.** (13 pts) For these, you need to fill in the box with the starting material or reagents as appropriate. Note, this is **NOT** a synthesis problem, the product can contain carbon atoms from your reagent!

Cianatura	D <sub>0</sub> 12	(8)
Signature	rg 13	(0)

15. (8 pts) Here is a synthesis warm-up. For the following series of reactions, we have given you the final product and starting material. Work backwards and in the box provided write the missing reagents. Note: we gave you the first two

Pg 14 \_\_\_\_\_(10)

16. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. All the carbons of the product must come from carbons of the starting material.

Signature	Ρσ 15	(16)
Signature	rg 13	(10)

**16.** (cont.). These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. All the carbons of the product must come from carbons of the starting material.