NAME (Print):	:	 Fin	emistry 320N al Exam
EID		Ma	y 3, 2024
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 during your organic chemistry journey. 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!!!

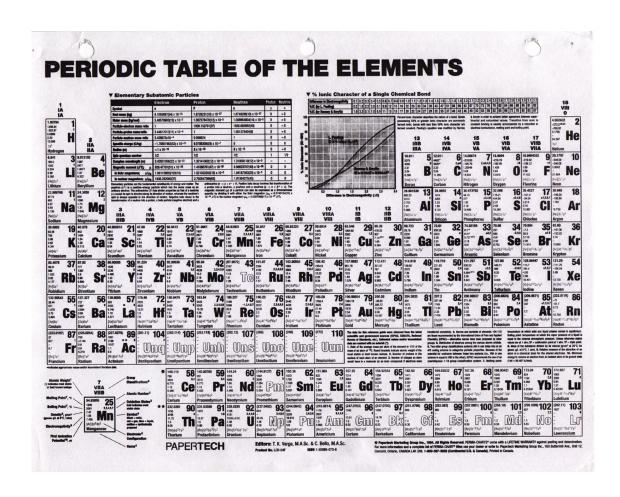
Student Honor Code for the University of Texas at Austin

"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)



Compo	ound	рК _а
Hydrochloric acid	<u>H</u> -Cl	-7
Protonated alcohol	⊕ RCH ₂ O <mark>H₂</mark>	-2
Hydronium ion	<u>H</u> ₃O [⊕]	-1.7
Carboxylic acids	O R-CO- <u>H</u>	3-5
Thiols	RCH₂S <mark>H</mark>	8-9
Ammonium ion	$\mathbf{\underline{H}}_{4}N^{\bigoplus}$	9.2
β-Dicarbonyls	O O RC-C <mark>H</mark> 2·CR'	10
Primary ammonium	H ₃ NCH ₂ CH ₃	10.5
β-Ketoesters	O O RC-C <u>H</u> 2-COR'	11
β-Diesters	O O ROC-C <u>H</u> 2·COR'	13
Water	HO <mark>H</mark>	15.7
Alcohols	RCH ₂ O <u>H</u>	15-19
Acid chlorides	RC <mark>H₂-CCI</mark>	16
Aldehydes	RC <u>H₂</u> -CH	18-20
Ketones	RC <u>H</u> ₂ -CR'	18-20
Esters	O RC <mark>H</mark> 2-COR'	23-25
Terminal alkynes	RC≡C— <mark>H</mark>	25
LDA	\underline{H} -N(<i>i</i> -C ₃ H ₇) ₂	40
Terminal alkenes	R ₂ C=C-H	44
Alkanes	CH₃CH₂- <u>H</u>	51

Golden Rules of Chemistry for your reference

A. Predicting Structure and Bonding 1. In most stable molecules, all the atoms will have filled valence shells. 2. Five- and six-membered rings are the most stable. 3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties 4. The most important question in organic chemistry is "Where are the electrons?" 5.

Delocalization of charge over a larger area is stabilizing. 6. Delocalization of unpaired electron density over a larger area is stabilizing. 7. Delocalization of pi electron density over a larger area is stabilizing. C. Predicting Reactions 8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough. 9. Functional groups react the same in different molecules. 10. A reaction mechanism describes the sequence of steps occurring during a reaction. 11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

Hello everyone, my name is 2-(4-((3,5-di(but-1-yn-1-yl)phenyl)ethynyl)-2,5-bis(3,3-dimethylbut-1-yn-1-yl)phenyl)-1,3-dioxolane. I understand that your class absolutely crushed the 3.1 mile challenge so that there is no nomenclature on this final exam. That is awesome and I hope you noticed how exercise resets your brain chemistry for better mental health while providing a path toward better overall health and fitness!

We are here at the end of your OChem experience. *I have been honored to be on this journey of learning and discovery with you*. You started by learning about molecular structure and bonding in OChem 1 and now you can carry out sophisticated syntheses to make complex molecules from simpler ones. That technology, the ability to make and break specific chemical bonds, has created what we know as modern life. And now you understand how it works. But that is not all. You also have a solid foundation for understanding the structure and reactivity of the very molecules that are responsible for life on this planet.

And if you have gone through my previous finals you have seen this poem before, but I want you to read this on your own final exam. This is to you, my sincere wish, taken from the words of one of the great poets of the 20th Century, Bob Dylan.

Here is my original first verse, written specifically for each of you:

"Every chance you get, You should go out for a run, That is the very best way For you to stay forever young."

"May your wishes all come true May you always do for others And let others do for you May you build a ladder to the stars And climb on every rung May you stay forever young

May you always know the truth And see the light surrounding you May you always be courageous Stand upright and be strong May you stay forever young

May your hands always be busy May your feet always be swift May you have a strong foundation When the winds of changes shift May your heart always be joyful May your song always be sung And may you stay forever young"



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!

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. You do **not** have to put arrows on any of the structures.



4. (1 pts each). Each of the following structures is either aromatic, not aromatic, or anti-aromatic. Fill in the circle that best describes each of the following structures. Note that on the following structures, some H atoms are drawn for the sake of clarity, while others are assumed to be present but are not drawn.



- **○**Aromatic ONot aromatic
- **○**Anti-aromatic



- **○**Aromatic ONot aromatic
- OAnti-aromatic



- **○**Aromatic
- **○**Not aromatic **Anti-aromatic**



- **○**Aromatic
- Not aromatic OAnti-aromatic



- **Aromatic** ONot aromatic
- Anti-aromatic



- **O**Aromatic ONot aromatic
- **Anti-aromatic**



- **Aromatic** ONot aromatic
- **OAnti-aromatic**



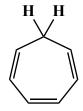
- **O**Aromatic
- **○**Not aromatic **Anti-aromatic**



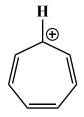
- **Aromatic**
- ONot aromatic **Anti-aromatic**



- **Aromatic ○**Not aromatic
- **Anti-aromatic**



- **Aromatic**
- ONot aromatic **Anti-aromatic**



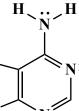
- **Aromatic**
- ONot aromatic **Anti-aromatic**



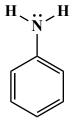
- **Aromatic** ONot aromatic
- **Anti-aromatic**

Adenine

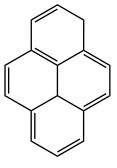




- **○**Aromatic ONot aromatic **Anti-aromatic**



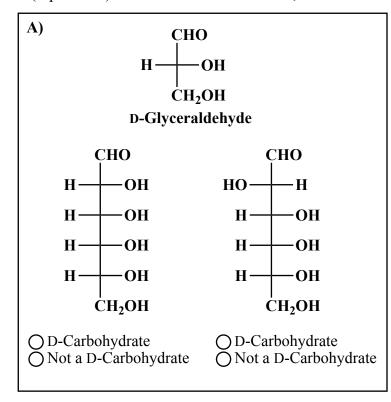
- **Aromatic ○**Not aromatic
- **OAnti-aromatic**



- **○**Aromatic **○**Not aromatic
- Anti-aromatic

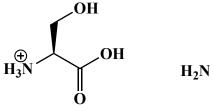
○Not aromatic **○Anti-aromatic** **5.** (2 pts each) For each arrow, on the line provided write the hybridization state of the atom indicated. Appropriate answers might be sp, sp², or sp³.

6. (2 pts each) For each set of molecules, fill in the circles that correctly describe the situation.



7. (2 pts each) For each set of molecules, fill in the circle corresponding to the answer that correctly describes the situation.

The p K_a of R-NH₃ is about 10 A. The p K_a of R-CO₂H is about 3.5 The pK_a of R-CH₂OH is about 16



- OH. H_2N
- OH

This is correct for pH 2.0 This is correct for pH 7.0

This is correct for pH 10.0

Can be used as a base

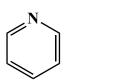
Not a base

This is never correct

- This is correct for pH 2.0 This is correct for pH 7.0

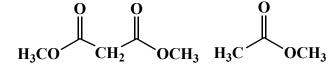
 - This is never correct
- This is correct for pH 2.0 This is correct for pH 7.0
- This is correct for pH 10.0 This is correct for pH 12.0 This is correct for pH 10.0
 - This is never correct
- This is correct for pH 2.0 This is correct for pH 7.0
- This is never correct

B.



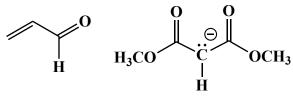
- Can be used as a base
- Not a base

C.



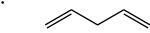
- \bigcap Lower p K_a Higher pK_a
-) Lower p K_a Higher pK_a

D.



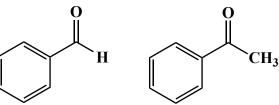
- Can be an electrophile in a Michael reaction
 - Can be a nucleophile in a Michael reaction
- Can be an electrophile in a Michael reaction
- Can be a nucleophile in a Michael reaction

E.



- A conjugated diene Not a conjugated diene
- A conjugated diene Not a conjugated diene

F.



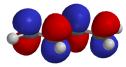
- Can make an enolate
- Cannot make an enolate
- CH₃
- O Can make an enolate
- Cannot make an enolate

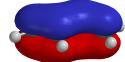
- G.
 - Reactive conformation in a decarboxylation reaction
 - Not a reactive conformation in a decarboxylation reaction
- Reactive conformation in a decarboxylation reaction
- Not a reactive conformation in a decarboxylation reaction

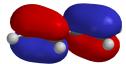
8. (16 pts) Yep, this exact problem was on the 3rd midterm except this time we shuffled the locations of the different orbitals. We wanted to give you the opportunity to improve how you did on this! The following are the pi molecular orbitals for 1,3-butadiene. Under each one place a number corresponding to energy, with a "1" under the lowest energy (most stable) molecular orbital, a "4" under the highest energy (least stable) molecular orbital and a "2" and a "3" as appropriate.

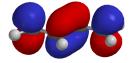


1,3-Butadiene









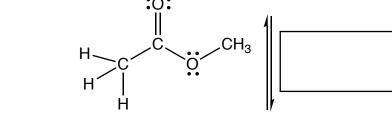
B) On the lines below, write "bonding" or "antibonding" as appropriate to describe the orbitals above:

C) On the lines below, write how many electrons are in each orbital BEFORE a photon is absorbed:

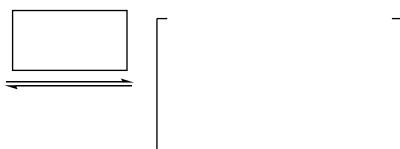
D) On the lines below, write how many electrons are in each orbital immediately AFTER a photon is absorbed (before the energy is lost as heat):

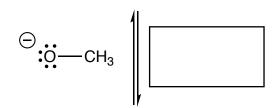
9. (9 pts) Draw all three of the other important contributing structures of the following arenium ion intermedate. Make sure to draw all lone pairs and formal charges. You do **not** have to put arrows on any of the structures.

10. (30 pts) Complete the mechanism for the following Claisen reaction. Be sure to show 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 OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

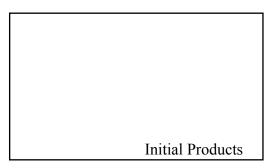








(Chemist opens flask and adds a mild acid)



Final Products

11. (26 pts) Complete the mechanism for the following Michael reaction. Be sure to show 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 OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

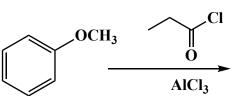
(No need to draw arrows on this structure)

Tautomerization

12. (3 or 5 pts.) Write the predominant product(s) 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. For these, you do not have to worry about metal salts in the products. For all aldol reactions, we only want you to draw the dehydrated products.

$$\begin{array}{c|c} & \text{NO}_2 & \text{HNO}_3 \\ \hline & \text{H}_2\text{SO}_4 \end{array}$$

$$\begin{array}{c|c}
& Br_2 \\
\hline
& FeBr_3
\end{array}$$



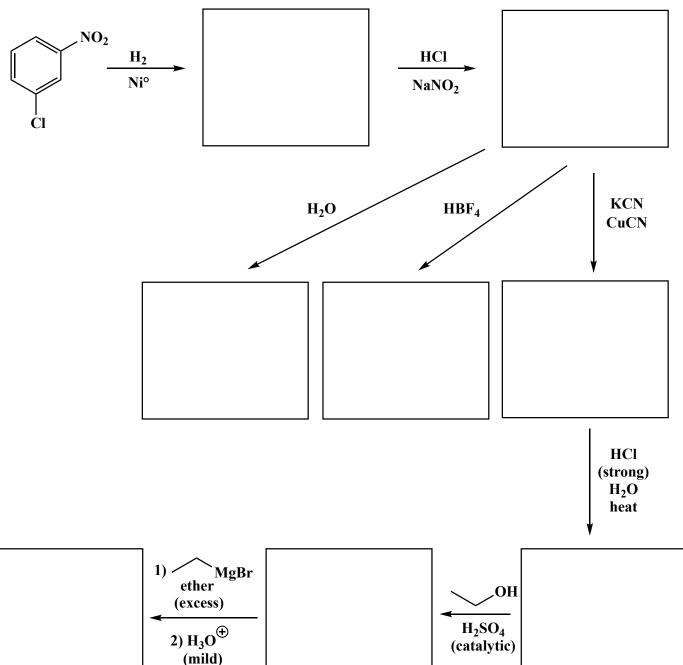
$$Cl$$
 Br_2 $FeBr_3$

$$\begin{array}{c} \text{NO}_2 \\ \hline \\ \text{OCH}_3 \end{array}$$

NO ₂ HNO ₃ H ₂ SO ₄	
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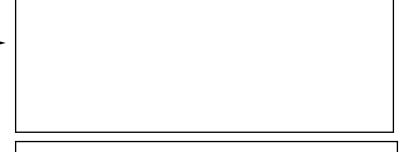
12 (cont.). (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges () and dashes () to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. For all aldol reactions, we only want you to draw the dehydrated products.



12 cont. (3 or 5 pts.) Write the predominant product(s) 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. For these, you do not have to worry about metal salts in the products. For all aldol reactions, we only want you to draw the dehydrated products.

$$\begin{array}{c} O \\ \hline \\ H_2N-NH_2 \\ \hline \\ KOH \end{array}$$

$$\bigcap_{H} \bigcap_{\Theta} P(Ph)_3$$

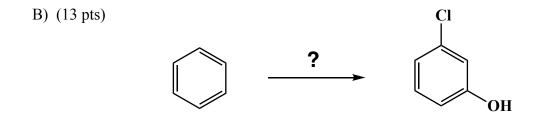


12 cont. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges () and dashes () to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. For all aldol reactions, we only want you to draw the dehydrated products.

12 cont. (3 or 5 pts.) Write the predominant product(s) 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. For these, you do not have to worry about metal salts in the products. For all aldol reactions, we only want you to draw the dehydrated products.

Signature	D ₀ 12	(1)
Signature	rg 15	(4)

 Pg 14	(13
	Pg 14



Signature	Pg 15	(21)
<u> </u>	1515	(21)

C) (21 pts)
$$CH_3CI$$

$$RO_2$$

$$RO_2$$

$$RO_2$$

$$RO_2$$

(10)

Signature	Pg 17	(16)
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14. (8 pts) Here is an "apply what you know" problem with an important message. Monday, April 29th, 2024, KXAN News reported 30 overdoses in Austin, resulting in 4 deaths. The individuals who survived were saved by the use of Naloxone, also known as Narcan. The fentanyl opioid crisis is far deadlier than any other substance abuse problem we have ever faced because fentanyl is too easy to make and too potent. Two milligrams is the difference between life and death for people using fentanyl. The other difference is that fentanyl is being sold to young people as Xanax and other legimate medications used to treat anxiety, complete with very realistic looking pills intended to look like authentic Xanax. There is no such thing as black market authentic Xanax, it is all some binding substance laced with a small amount of fentanyl. Too many doses will take unsuspecting consumers into full opioid addiction, leading to catastrophic personal consequences. And one dealer accidentally adding 0.5 mg too much to each pill could kill everyone taking them, unless someone nearby has Narcan, the spray bottle form of Naloxone. Two squirts of Narcan in each

nostril will save the life of an unconcious person who had taken a fatal overdose of fentanyl. The reason this works is that Naloxone is an extremely potent derivative of morphine that binds very tightly to the same opioid receptor as morphine, heroine and fentanyl. Unlike the three opioids, Naloxone does **not** activate the receptor, it just binds and blocks morphine, heroine or fentanyl from binding and causing receptor activation. Naloxone is referred to as an *antagonist*, while morphine, heroine and fentanyl are *agonists*.

Recall that a key principle behind organic chemistry is that functional groups react the same in complex molecules as they do in simpler ones.

Naloxone is relatively inexpensive because it is made in few steps from morphine or other natural derivatives, an approach called "semi-synthesis". You have not seen all of the steps involved in synthesizing Naloxone from morphine, but you have seen a couple of them.

1. An early step in the conversion of morphine to Naloxone involves making an ester on the OH group attached to the aromatic ring using acetic anhydride.

An interesting feature of this reaction is that only one of the two OH groups on the starting molecule reacts. The OH group indicated by the arrow does **not** react even though an excess of acetic anhydride is used. **Select the single answer that best explains why the OH group indicated by the arrow does <u>not</u> react with acetic anhydride in this reaction:**

- The tertiary alcohol (the OH indicated by the arrow) has too much steric hindrance around it.
- The aromatic OH group (the one that reacts) is just a better electrophile.
- The aromatic OH group (the one that reacts) has more steric hindrance around it.
- \bigcirc The N atom nearby makes the tertiary alcohol (the OH indicated by the arrow) too much of an electrophile.

2. In one published synthesis of Naloxone (Adv Synth. Catal. **2013**, *355*, 1869 – 1973), this is the very last step:

Select from the following reaction conditions and indicate the one set of conditions that is the most appropriate for this step:

- (1) NaBH_{4.} 2) H₂O
- O H₂CrO₄
- O H₂O (excess) HCl (catalytic) heat
- OCH₃OH (excess) HCl (catalytic) heat

Remember, you can get a dose of Narcan at the PCL circulation desk. It is free of charge and no questions will be asked. Please do this. **You could save a life.** A former student in the class took my advice and saved their brother's life because when it was needed, they happened to have the very same dose of Narcan I had told them how to obtain from PCL.