NAME (Print): _____

Chemistry 320N 3rd Midterm Exam April 17, 2025

EID

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

"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."



Compound		рК _а
Hydrochloric acid	H-CI	-7
Protonated alcohol	⊕ RCH₂O <mark>H₂</mark>	-2
Hydronium ion	<u>H</u> ₃O [⊕]	-1.7
Carboxylic acids	∥ R−CO- <u>H</u>	3-5
Thiols	RCH₂S <mark>H</mark>	8-9
Ammonium ion	H₄N⊕	9.2
β -Dicarbonyls	0 0 RC-C <mark>H</mark> 2·CR'	10
Primary ammonium	H ₃ NCH₂CH ₃	10.5
β-Ketoesters	OO B RC-C <u>H</u> 2 [·] COR'	11
β -Diesters	000 ROC-C <mark>H</mark> 2·COR'	13
Water	HOH	15.7
Alcohols	RCH ₂ O <u>H</u>	15-19
Acid chlorides	O RC <u>H</u> 2-CCI	16
Aldehydes	RC <u>H</u> 2-CH	18-20
Ketones	RC <u>H</u> 2-CR'	18-20
Esters	U ∥ RC <u>H₂</u> -COR'	23-25
Terminal alkynes	RC≡C— <u>H</u>	25
LDA	<u>H</u> -N(<i>i</i> -C ₃ H ₇) ₂	40
Terminal alkenes	R₂C≕C— <u>H</u> H	44
Alkanes	CH₃CH₂- <mark>H</mark>	51

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

Where are the electrons?

2. (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.)



No question here, just decipher the OChem puns!



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3. (2 pts each) Fill in the appropriate circle to indicate if the statement is True or False		
TrueFalse	For a reaction that is under thermodynamic control, the major product is the product that is lower in energy.	
TrueFalse	For a reaction that is under thermodynamic control, the major product is the product that is derived from the lower energy intermediate.	
TrueFalse	For a reaction that is under kinetic control, the major product is the product that is lower in energy.	
TrueFalse	For a reaction that is under kinetic control, the major product is the product that is derived from the lower energy intermediate.	
TrueFalse	An enamine can be formed when a secondary amine reacts with a ketone or aldehyde at pH 4.	
TrueFalse	Enamines can be alkylated by reaction with primary haloakanes, or acylated by reaction with acid chlorides.	
TrueFalse	Molecules appear to our eye to be a combination of the wavelengths reflected (not absorbed)	
TrueFalse	Molecules appear to our eye to be a combination of the wavelengths absorbed (not reflected)	
TrueFalse	The greater the number of pi bonds in conjugation, the larger the energy difference between filled and unfilled orbitals, so the shorter the wavelength of light that is absorbed.	
TrueFalse	The greater the number of pi bonds in conjugation, the smaller the energy difference between filled and unfilled orbitals, so the longer the wavelength of light that is absorbed.	
TrueFalse	Phosphorescence (glow in the dark) happens when the excited electron has flipped spins, and must reflip back before entering the original filled orbital while emitting a photon.	
TrueFalse	Fluorescence occurs when there are not vibrations possible (a rigid molecule) so the photon is emited as the electron goes back to ground state.	
TrueFalse	Atoms with a positive charge, a negative charge or an unpaired electron are all highly stabilized by resonance delocalization when attached directly to an aromatic ring.	

4. (26 pts) The following molecules are best represented as the hybrid of contributing structures. **Draw the other important contributing structure(s)** in the space(s) provided, including all lone pairs and formal charges. **For the structure(s) on the left, use arrows to indicate the movement of electrons to give the structure you drew.** No arrows for the structures on the right.



5. (2 pts each) For each pair of molecules, fill in the circle to indicate which one is the stronger acid.



6. (2 pts each) For each of the following molecules we have seen in reaction mechanisms, fill in the circle to indicate whether the molecules acts as a nucelophile or electrophile. For this one, you can ignore acid or base considerations and just focus on the nuclophile/electrophile properties of the molecules.



7. (1 pt each) Indicate whether each of the following molecules and ions is aromatic or not aromatic by filling in the appropriate circle. H



8. (1 pt each) For each arrow, on the line provided write the type of atomic of bital that contain (2^{3}) the lone pair of electrons indicated. Appropriate answers might be sp, sp², sp³ or 2p.



9. (1 pt each) For each arrow, on the line provided write the hybridization state of the atom indicated. Appropriate asnwers might be sp, sp², or sp³.



10. (9 pts) Complete the following mechanism. Be sure to show arrows to indicate movement of all electrons of the first structure only, 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 OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE.





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11. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown <u>to completion</u>. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.



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12. (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.).

__(26)



13. (3 or 5 pts.) Write the predominant product 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.



14. (3 or 5 pts.) Write all of the organic 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 need to write all of the products of the reactions except for the products containing metals.



15. (7 or 9 pts.) Write all of the organic 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 need to write all of the products of the reactions except for the products containing metals.



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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. For this exam you do not need to draw each stereoisomer with wedges and dashes, you can just mark all chiral centers with an asterisk and write "racemic" when appropriate. All the carbons of the product must come from carbons of the starting material.



Recognize that the product is an ester with 9 carbon atoms, and the starting material has 3 carbon atoms. Therefore, three starting material molecules will be combined in the product. **Recognize** the product as a β -keto ester, the KRE of a Claisen. Therefore propose the last step is a Claisen reaction with the corresponding 6 carbon ester as shown. The 6 carbon ester can be made from the starting 1-propanol through the familiar sequence of oxidation to the carboxylic acid, reaction with SOCl₂ to give the acid chloride and reaction with 1-propanol to give the desired ester.



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Recognize that the product has 8 carbon atoms and the starting material has 4 carbon atoms. Therefore, two starting material molecules will be combined in the product. **Recognize** the product as an α , β -unsaturated aldehyde with the new C=C bond as shown, the KRE of an aldol reaction followed by dehydration. Therefore propose the last step is the dehydration reaction of the corresponding β -hydroxy aldehyde, the product of an aldol reaction with butyraldehyde as shown. Butyraldehyde can be made from the starting 1-butene by the non-Markovnikov hydroboration reaction followed by PCC.

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.



Recognize that the product and starting material both have 6 carbons. **Recognize** that the product is an α,β -unsaturated aldehyde, the KRE of an aldol reaction followed by dehydration. Therefore propose the last step is the dehydration of the corresponding β -hydroxy aldehyde. **Recognize** further that the product is a five-membered ring while the starting material is a six-membered ring, indicating the starting six-membered ring must be opened up somehow. Putting it all together, propose that the aldol reaction uses hexane dial, that is made by ozonolysis of the starting cyclohexene.





Recognize that the product is an ester with 7 carbon atoms, and the starting materials has 4 carbon atoms and 2 carbons, no much help here other than telling you there will be two new carbon-carbon bonds made somehow. Recognize the product as a methyl ketone, the KRE of an acetoester synthesis. **Recognize** further that the product has a new carbon-carbon bond that is at the β -carbon of the aldehyde carbonyl on the other end of the molecule, the KRE of a Michael reaction. **Recognize** the acetoester as the nucleophile for the Michael reaction. Therefore propose the last step is an ester hydrolysis /decarboxylation after a Michael reaction using the α , β -unsaturated aldehyde derived from the starting acetaldehyde through an aldol followed by dehydration. The acetoester is made from the starting ethyl acetate via a Claisen reaction.