NAME (Print):	 Chemistry 320N Dr. Brent Iverson
SIGNATURE:	 2nd Midterm March 23, 2017
Please print the	

Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. I recommend you look the exam over and answer the questions you are sure of first, then go back and try to figure out the rest. Also make sure to look

at the point totals on the questions as a quide to help budget your time.

first three letters of your last name in the three boxes

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS 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. PLEASE PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points	
1		(34)
5		(18)
6		(22)
7		(12)
8		(24)
9		(35)
10		(34)
11		(14)
12		(22)
13		(19)
14		(13)
15		(22)
16		(13)
17		(10)
Total		(292)

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."

(Your signature)

Comp	ound	рК _а
Hydrochloric acid	H-Cl	-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	<u>H</u> ₄N [⊕]	9.2
β -Dicarbonyls	0 0 RC-C <mark>H</mark> 2 ⁻ CR'	10
Primary ammonium	H_3 NCH ₂ CH ₃	10.5
β -Ketoesters	0 0 RC-C <u>H</u> 2 [·] COR'	11
β -Diesters	0 0 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>H₂</u> -CCI	16
Aldehydes	0 RC <u>H</u> 2-CH	18-20
Ketones	RC <u>H₂</u> -CR'	18-20
Esters	∥ 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

DO NOT TEAR OUT THIS PAGE!!

You must write the answers for the questions on the next four pages on this single sheet.

Question 1, page 2 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of reactivity of the molecules, listed from most to least reactive.

Question 2, page 2 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of reactivity, listed from most to least reactive.

Question 3, page 3 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of acidity, listed from most to least acidic.

Question 4, page 3 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of acidity, listed from most to least acidic.

Question 5, page 4 (5 pts) Write the hybridization state of the atoms indicated by the arrows.

5.1 5.2 5.3 5.4 5.5

Question 6, page 4 (6 pts) Write "can rotate" or "cannot rotate" corresponding to whether the bond indicated by the arrows can rotate or cannot rotate freely at room temperature.

 6.1
 6.2
 6.3

 6.4
 6.5
 6.6

Question 7, page 4 (3 pts) Is the fragment of cobra toxin shown as it would exist at very high pH or very low pH?

1. (5 pts) Rank order all of the following with respect to reactivity with a nucleophile such as water at neutral pH. **On the answer sheet on page 1 write the letter corresponding to the correct order of reactivity,** ranked from most to least reactive for the molecules labeled as (a) - (d).



2. (5 pts.) Rank order all of the following with respect to reactivity with a nucleophile such as water at neutral pH. **On the answer sheet on page 1 write the letter corresponding to the correct order of reactivity**, ranked from most to least reactive for the molecules labeled as (a) - (c).



Pg 2 _____(10)

Write the answers to these questions on the answer sheet on page 1

3. (5 pts) Rank the following molecules with respect to overall acidity. **On the answer sheet on page 1, write the letter corresponding to the correct order of acidity,** ranked from most to least acidic for the molecules labeled as (a) - (d).



4. (5 pts) Rank the following molecules with respect to overall anion stability. **On the answer sheet on page 1, write the letter corresponding to the correct order of anion stability,** ranked from most to least stable for the anions labeled as (a) - (d).



most stable			least stable		
A)	(a)	(c)	(b)	(d)	
B)	(a)	(b)	(d)	(c)	
C)	(c)	(a)	(b)	(d)	
D)	(d)	(c)	(a)	(b)	
E)	(d)	(b)	(c)	(a)	

Write the answers to these questions on the answer sheet on page 1

5 (5 points) On the answer sheet on page 1, indicate the **hybridization state of each atom identified** by the arrows.



Saquinavir - An effective treatment for AIDS (AIDS protease inhibitor)

6. (6 points) On the answer sheet on page 1, indicate whether the indicated C-N bond can or cannot rotate at room temperature.



These are the last four amino acids of one of the most potent Egyptian cobra toxins

7. (3 points) On the answer sheet on page 1, indicate whether the above cobra toxin fragment is shown in very high (greater than 12) or very low (less than 2) pH?



8. (18 pts) In a bond-making step of a reaction, a nucleophile donates the electron pair that will make the new bond, and an electrophile accepts the electron pair in the process. The following species are either nucleophiles or electrophiles in reaction mechanisms we have learned. Note for this problem we are ignoring any proton transfer steps, we are just interested in whether the following can best be considered a nucleophile or an electrophile. **ON THIS PAGE CIRCLE "nucleophile" or "elctrophile"** to indicate the reactivity of each structure.



9. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

10. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



11. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



12. (4 pts) In the space provided, draw the following molecule: isopropyl (*R*)-2-hydroxy-4-pentenoate



Latin Name: (3Z,4aZ,6Z,11aZ,13Z,14Z)-3,8,10,15-tetra-*tert*-butyl-9-hexyl-1a,1b,1c,2a,15a,16a,16b,16c-octahydro-1*H*,9*H*-cyclohepta[9,10]octaleno[3,4*b*]cyclopropa[3',4']cyclobuta[1',2':3,4]cyclobuta[1,2-*e*][1,4]dioxine

Pg 8 _____(24)

Signature

Draw arrows on this structure

Note you will have to write a balanced equation for the above mechanism on page 11

14. (12 pts) Complete the mechanism for the following reaction a lactone and hydroxide. 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.).



Note you will have to write a balanced equation for the above mechanism on the page 11

15. (35 pts) Complete the mechanism for the following ester hydrolysis 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. 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.).



Note you will have to write a balanced equation for the above mechanism on PAGE 11

16. (34 pts) Complete the mechanism for the following Wolff-Kishner 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.).



Note you will have to write a balanced equation for the above mechanism on PAGE 11

17. (14 pts) Write BALANCED equations for the four mechanisms, 1-4, that you drew on the last three pages. Only include molecules consumed or created during the reactions. In other words, DO NOT SHOW CATALYSTS IN EITHER BOX!

Write a balanced equation for the overall process described by mechanism 1 from page 8



Write a balanced equation for the overall process described by mechanism 2 from page 8

Write a balanced equation for the overall process described by mechanism 3 from page 9

Write a balanced equation for the overall process described by mechanism 4 from page 10





18. (3 or 5 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.



19. (3 or 5 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. Also, do not worry about balancing these equations, you just need to show us the major organic products of these transformations.

$ \underbrace{)}_{Cl}^{O} \underbrace{)}_{2}^{CuLi} \underbrace{)}_{2}$	
$\frac{O}{NH_2} = \frac{1) \text{ LiAlH}_4}{2) \text{ H}_2 O}$	
$\begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 1 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 2 \\ 1 \\ 2 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 0 \\ 0 \\ \end{array}$ $\begin{array}{c} 1 \\ 0 \\ 0 \\ \end{array}$	Draw all the carbon containing products made from the ester starting material
$N = C_{H_1,} O = C_{H_2,} O = C_{H_2,.$	Draw all the carbon containing products made from the ester starting material
$(1) 2 eq.$ (H_3MgBr) $(1) 2 eq.$ (H_3MgBr) (H_2O) $(mild acid)$	Draw all the carbon containing products made from the ester starting material

20. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

Remember, all of the carbons of the product must come from the given starting material.

(13 pts)



racemic

Signature____

20. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

Remember, all of the carbons of the product must come from the given starting material.

(22 pts)



20. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

Remember, all of the carbons of the product must come from the given starting material.

(13 pts)



21. Gleevec (also called imatinib) is the first example of a class of drugs known as TKI's, which stands for tyrosine kinase inhibitors. TKI's inhibit rogue enzymes that enable the "out of control" growth of certain cancers, such as several kinds of leukemia. The last step in the synthesis of Gleevec involves chemistry you know. Draw the structure of Gleevec in the box provided based on the reagents used in the last step of its synthesis.



22. As part of his research in my laboratory, your TA Chris needs to make an interesting molecule using the chemistry shown below. You know all the chemistry involved, or at least chemistry that is similar. Draw the product of the following step, which produces the molecule Chris will need to make what we hope will be an entirely new class of responsive liquid crystals. You only need to show the main (largest) carbon containing product, not all of the products of this process. Hint: Four reactions take place under these conditions and the product is a racemic mixture. You do not need to use wedges and dashes to indicate chirality BUT YOU MUST INDICATE EACH CHIRAL CENTER WITH AN ASTERISK (*).

