SIGNATURE:		 Chemistry 310N Dr. Brent Iverson Final May 12, 2007		
		ı	1	Ī
	Please print the first three letters of your last name in the three boxes			

NIA BAE (Duina)

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 guide to help budget your time.

For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IS IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT

Note: You must have your answers written in pen if you want a regrade!!!!

Page	Points	
1		(36)
2		(18)
3		(26)
4		(16)
5		(21)
6		(38)
7		(18)
8		(31)
9		(33)
10		(31)
11		(29)
12		(25)
13		(21)
14	,	(29)
15		(14)
16		(16)
17		(10)
18		(16)
19		(34)
Total		(462)
HW		
T Score		

Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom,
leadership, individual opportunity, and responsibility. Each member of the University is
expected to uphold these values through integrity, honesty, trust, fairness, and respect
toward peers and community.

(Your signature)

It has been a pleasure getting to know you this semester. Based on your performance on the three midterms, we think you are clearly the best class we have ever had at the University of Texas. I hope that you found this final to be challenging, but fair.

It is the sincere wish of the TA's and myself that you look back on your organic chemistry courses with a sense of pride on how far you have come in two semesters. Whereever your careers take you, we hope you now have the intellectual tools to identify, analyze, and understand molecules.

Have a safe summer and remember to excercise every chance you get. If you stay in shape, you will thank yourself more than you can imagine in a few years!!!

Brent Iverson

Comp	ound	pK _a
Hydrochloric acid	<u>H</u> -Cl	-7
Protonated alcoho	⊕ 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
Ammonium ion	<u>H</u> ₄N [⊕]	9.2
β-DicarbonyIs	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO	10
β-Ketoesters	RC-CH ₂ -COR'	11
β-Diesters	O O ROC-C <mark>H</mark> 2-COR'	13
Water	HO <u>H</u>	15.7
Alcohols	RCH ₂ O <u>H</u>	15-19
Acid chlorides	RC <mark>H₂-</mark> CCI	16
Aldehydes	₩ RC <mark>H</mark> ₂-CH	18-20
Ketones	RC <u>H₂</u> −CR'	18-20
Esters	O RC <mark>H₂-</mark> COR'	23-25
Terminal alkynes	RC≡C— <u>H</u>	25
LDA	\underline{H} -N(<i>i</i> -C ₃ H ₇) ₂	40
Terminal alkenes	R ₂ C≔C− <mark>H</mark> H	44
Alkanes	CH ₃ CH ₂ - <mark>H</mark>	51

1. (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 minumum of 7 key points here.

2. (10 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. We drew templates to save you time.

3. (12 pts) Because of pi delocalilzation, many of the atoms in the molecules below are predicted to be in the same plane. On the structures below, circle all the atoms that you believe will be located the same plane at all times. Do not circle atoms that are in the same plane only temporarily as bonds rotate freely at room temperature.

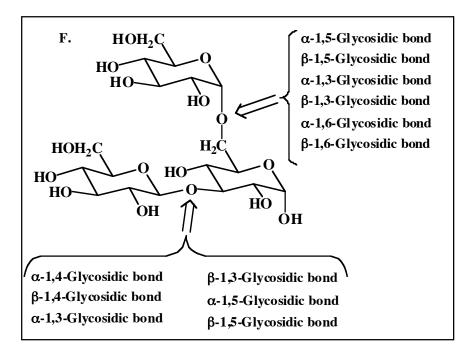
4. (11 pts) In the boxes provided, write the hybridization state of the given atoms.

5. (7 pts) In the boxes provided, according to the valence bond approach, write the type of atomic orbital that contains the indicated lone pair of electrons.

Signature	Pg 3		(26)
6. (2 pt. each) Here are a number of statements regarding general aspects of orga second guess yourself, this is not meant to be tricky! Check the appropriate box statement is true or false.			
		True	False
A. In ¹ H-NMR, a spectrum plots the energy (as frequency) necessary for the to be excited from the lower energy spin state to the higher energy spin state			
B. Equivalent hydrogen atoms in a molecule have an identical relationship t the other atoms in the molecule	o all		
C. Equivalent hydrogen atoms in a molecule give the same NMR signal.			
D. In $^1\mathrm{H} ext{-}\mathrm{NMR}$, the peaks are plotted using "ppm" as the units, which stands "proton peak measurement".	s for		
E. For alkyl groups with freely rotating bonds, complex splittings simplify be coupling constants ("J") are all about the same.	ecause		
F. In ¹ H-NMR, spin-spin splitting is caused by induced electron density mov that in turn induces small magnetic fields.	ement		
G. An α,β-unsaturead aldehyde is a great nucleophile in a Michael reaction.			
H. When a reaction is under thermodynamic control, only the relative energ the products determines which one predominates.	gies of		
I. When a reaction is under kinetic control, only the relative energies of the products determines which one predominates.			
J. The Diels-Alder reaction involves a two-step mechanism.			
K. The Diels-Alder reaction involves a concerted mechanism, with a transiti state, but no intermediates.	on		
L. In the Diels-Alder reaction, the stereochemistry of the dienophile (cis or to is maintained in the product.	rans)		
M. In the Diels-Alder reaction, the diene must be in the s-trans geometry			

7. (2 pts each) I know you were wondering how we were going to test the carbohydrate material. Here is what we came up with. For the following structures, draw a circle around the terms that provide the most accurate description.

E.
$$HOH_2C$$
 HO
 O
 HO
 OH
 α -D-Glucose
 β -D-Glucose
 β B β -D-Glucose
 Δ E-D-Glucose



Signature	e	

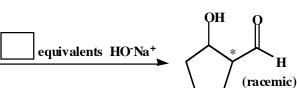
(racemic)

8. (11 points) A) This semester we have learned a great deal about carboxylic acids, guanidine groups, and amines. Here is an apply what you know problem. The so-called RGD peptides bind to special receptors in the body, including adhesion receptors important for angiogenesis (production of blood vessels). Charge is a major factor that controls binding of RGD peptides to their receptors. Below is th tripeptide Arginine-Glycine-Aspartic acid (RGD). In the boxes provided, draw the correct protonation state of the carboxylic acid, amine, or guanidine group at neutral pH, 7.0. You must show all protons and formal charges that are present on the functional groups within the four boxes. For this problem, assume the pK_a values of the carboxylic acids are 4.0, the pK_a value for a protonated amine is 9.2, and the pK_a value for a protonated guanidine group is 13.2.

- B) What is the total charge on this peptide at pH 7.0?
- C) What is the total charge on this peptide at pH 2.0?
- **D)** What is the total charge on this peptide at pH 11.2?

9. (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 to completion. 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.

$$\begin{array}{c} \ddot{O} & 2) \\ B) & O \\ H & O \end{array}$$



A)

10. (38 pts total) For the following, draw the other important contributing structure or structures (resonance form(s)) we presented in class. You must draw arrows on the structure to the left to indicate the flow of electrons that leads to the contributing structure you draw to the right (All but the rightmost structure on each line has arrows on it). Be sure to show all lone pairs and formal charges on your structures. We have drawn template structures to save you time.

11. (9 pts) Here is an apply what you know problem. One of the following esters reacts with nucleophiles such as primary amines thousands of times faster than the others. Circle the ester that reacts faster, and in the space provided, <u>in no more than two sentences</u> explain why it reacts faster.

Explain your answer here (no more than two sentences):

12. (9 pts) Here is another apply what you know problem. One of the following esters reacts MUCH MORE SLOWLY with NaOH. Circle the ester that does not react, and in the space provided, <u>in no</u> more than two sentences explain why it does not react.

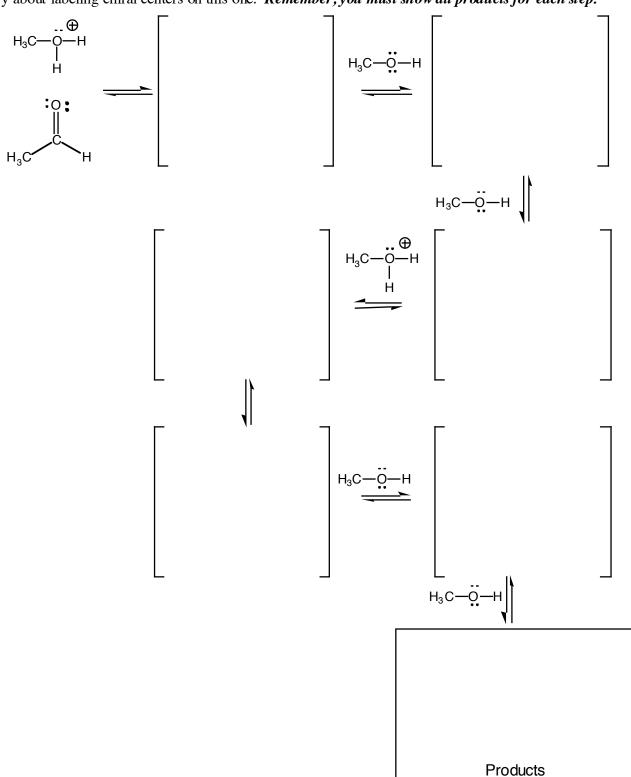
Explain your answer here (no more than two sentences):

Signature	Pσ S	(31)
Signature	1 g o	(31)

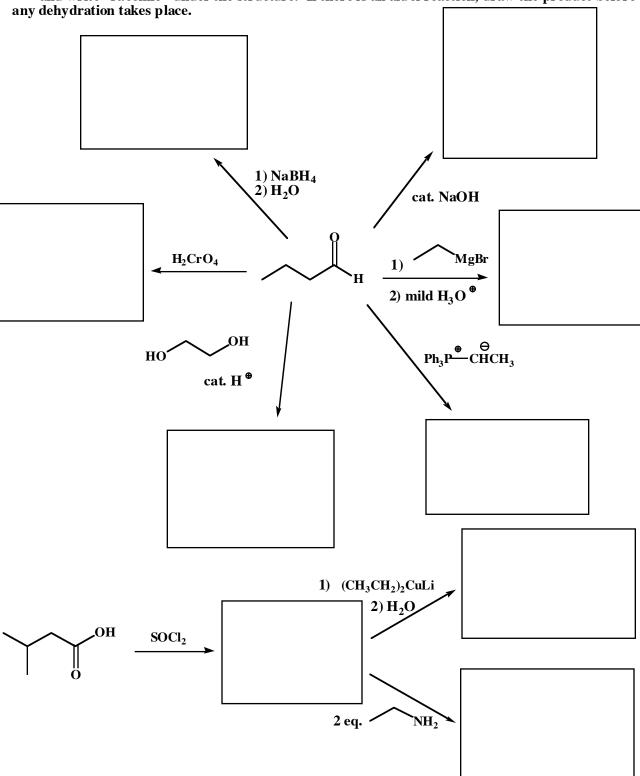
13. (31 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, 1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal charges and lone pairs on the intermediates. 3) Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate. 4) Finally, draw a box around the nucleophile and a circle around the electrophile in each case. There is no need to draw final products or any further steps of the mechanisms. You might want to read these directions again so you know what we want.

Did you remember to draw boxes and circles?

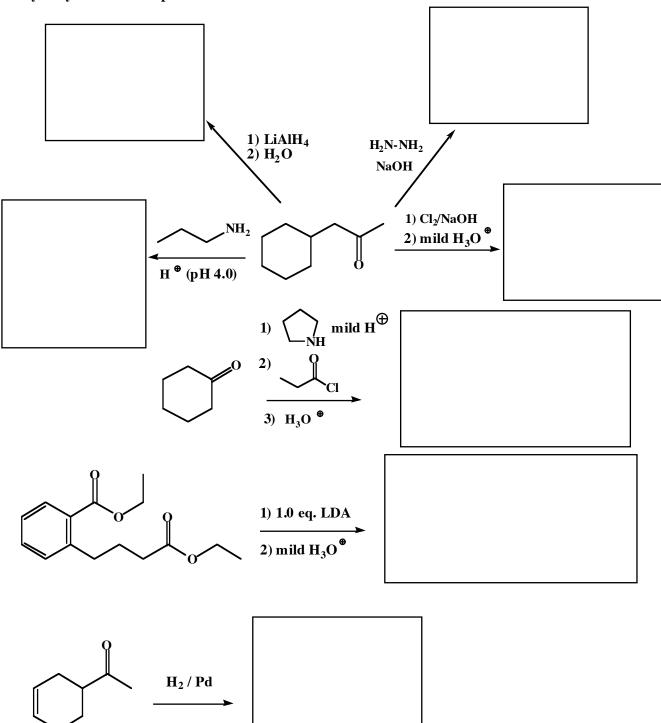
13. (33 points) Complete the mechanism below for acetal formation. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one. *Remember*, you must show all products for each step.



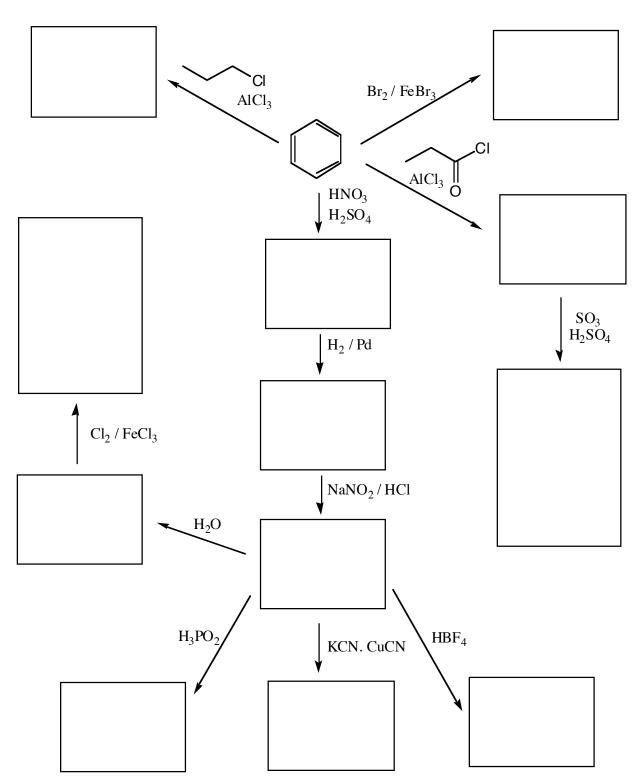
14. (31 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before



15. (29 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, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.



16. (25 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



17. (21 pts.) You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. If a new chrial center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, ald ols can dehydrate if heated in dilute acid.

$$\begin{array}{c|c}
\hline
 & 1) \text{ cat. NaOH} \\
\hline
 & 2) \text{ H}_3\text{O}^{\oplus}/\text{ heat}
\end{array}$$

Be sure to indicate stereochemistry of the products on this next one.

$$\begin{array}{c|c}
 & 1) 1.0 \text{ Eq. NaOEt} \\
\hline
 & 2) & Br \\
\hline
 & 3) \text{ H}_3 \text{O}^{\oplus}/\text{heat}
\end{array}$$

17. (21 pts.) Here is the synthesis of the important pharmaceutical Prozac. You are familiar with all of the chemistry, it just might take you a while to recognize the reactions. Fill in the boxes with the appropriate structures, and remember to use an asterisk "*" and write "racemic" to indicate any new chiral centers created along the way.

18. (8 pts) For the following reactions, circle the side of the equation that predominates at equilibriur

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(10 pts)
$$H$$
 OH $?$ NO₂

Signature	Pg 16	(16)

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! NOTE: For this one, you are not allowed to separate complex mixtures along the way and pull out just the isomers you want. In other words, the product isomers shown must be the only predominant isomers you make during your synthesis. This last restriction means you must think carefully about when you add the different group, even Mr. Bill might say "Oh no" to this one.

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Note, for these last two, you might not need to use all three starting materials

19. Using any reagents tum the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Note, for these last two, you might not need to use all three starting materials

(34 pts)