SIGNATURE:		Chemistry 310N Dr. Brent Iverson 1st Midterm Feb. 18, 2010			
	Please print the first three letters of your last name in the three boxes				

NIA REE (D : 1)

**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.

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 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!!!

Page	Points	
1		(13)
2		(19)
3		(18)
4		(15)
5		(5)
6		(5)
7		(5)
8		(5)
9		(5)
10		(14)
11		(22)
12		(18)
13		(20)
14		(12)
15		(16)
16		(10)
17		(15)
18		(13)
19		(28)
Total		(258)
%		
T Score		
HW		
Total Grade		

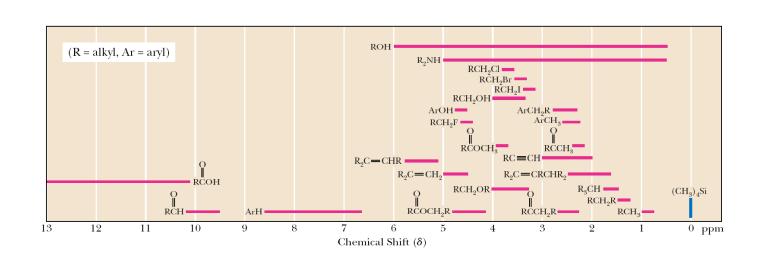
(HW score + Exam Grade) =

## **Honor Code**

The core values of the University of Texas	at Austin are learning, discovery, freedom,
11 3	consibility. Each member of the University is
expected to uphold these values through int	tegrity, honesty, trust, fairness, and respect
toward peers and community.	
-	(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
(K alkyl, Al alyl)	3HH (0)	(it uikyi, zii uiyi)	Sillit (0)
		RC <b>H</b> 2OH	3.4-4.0
R <sub>2</sub> N <b>H</b>	0.5-5.0	RCH <sub>2</sub> Br	3.4-3.6
RO <b>H</b>	0.5-6.0	RCH <sub>2</sub> Cl	3.6-3.8
RCH₃	0.8-1.0	Ö.	2.0 2.0
RCH <sub>2</sub> R	1.2-1.4	$R^{\square}_{OCH_3}$	3.7-3.9
R₃C <b>H</b>	1.4-1.7	0	
$R_2C=CRCHR_2$	1.6-2.6	RCOCH2R	4.1-4.7
RC≡C <b>H</b>	2.0-3.0	RCH₂F	4.4-4.5
0		ArOH	4.5-4.7
RCCH <sub>3</sub>	2.1-2.3	$R_2C=CH_2$	4.6-5.0
0		$R_2C=CHR$	5.0-5.7
RCC <b>H</b> 2R	2.2-2.6	Q	
ArC <b>H</b> 3	2.2-2.5	H <sub>2</sub> G-CH <sub>2</sub>	3.3-4.0
RCH <sub>2</sub> NR <sub>2</sub>	2.3-2.8	, J	0.5.10.1
RCH <sub>2</sub> I	3.1-3.3	R <b>CH</b>	9.5-10.1
RCH <sub>2</sub> OR	3.3-4.0	RCOH	10-13

<sup>\*</sup>Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



Signatur	re		Pg	g 1(13)
<b>1.</b> (1 pt e	each) Fill in each	blank with the word that bes	t completes the following	sentences about NMR.
The two	most important	isotopes for organic che	mistry structure deter	mination by NMR
are	and	Of these two,	is a common is	sotope and the
predomin	ant isotope fou	nd in molecules, while _	is relatively	rare.
Nuclei wi	ith spin quantu	n number 1/2 are quantiz	zed in one of two ories	ntations:
(lower en	ergy) or	(higher energy) in th	e presence of an exter	rnal magnetic field,
that is, wi	ith and against	the external field, respect	tively.	
strength o	of the magnetic	between nuclear spin st field experienced by the red to move in a strong ex	nucleus.	
movemen	nt induces a	field t	hat is	to the
external n	nagnetic field.	This has the effect of		the underlying
nuclei fro	m the external	magnetic field.		
All other	factors being th	ne same, the signal for an	<sup>1</sup> H atom with greater	electron density
around it	will come at _	pp	om in an NMR spectru	ım compared to a
similar <sup>1</sup> H	I atom with les	s electron density.		
The	(	of adjacent nuclei influen	ce each other. If <sup>1</sup> H a	atoms are no more
than	bon	ds apart, the spin states c	ouple.	

(19)
_

**1.** (**cont.**) (1 pt each)

In the FT NMR method, the FT stands for \_\_\_\_\_\_\_.

The basic idea is that a short pulse using a range of radio frequencies is used to flip the spins of all of the hydrogen \_\_\_\_\_\_ at once. Then, the nuclear spins \_\_\_\_\_\_ back to the +1/2 spin state and when they do, they \_\_\_\_\_\_ electromagnetic radiation at the precise frequency at which they absorb.

This is not part of a question. This little molecule creature is simply supposed to make you smile!

**2.** (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.

15. (13 pts total) I promised you this one!! For each set of reagents below, draw the key transition state that occurs during the reaction. Use dotted lines to indicate bonds that are in the process of being broken or made. Write all lone pairs and any formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.

A.

$$H-S: + H_3C C CH_3$$

Transition State

B.

$$H_{3}C - O : + H_{3}C = I :$$

$$H_{3}C - C = H_{3}C = I :$$

$$C - C =$$

16. (5 pts total) For the set of reagents below, draw the **first key intermediate** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key intermediate. Write all lone pairs and formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.

$$H-O: + H_3C C_{CH_3}$$

Hand  $H_3C C_{CH_3}$ 

Intermediate

**3.** (3 pts) The most important question in organic chemistry is:

**4.** (3 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

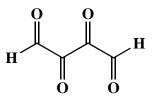
Α.

$$\begin{array}{ccc} \operatorname{Br} & \operatorname{O} \\ | & | | \\ \operatorname{CH}_3\operatorname{CH}_2\operatorname{CCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CCH}_3 \\ | & \operatorname{CH}_2\operatorname{CH}_3 \end{array}$$

B.

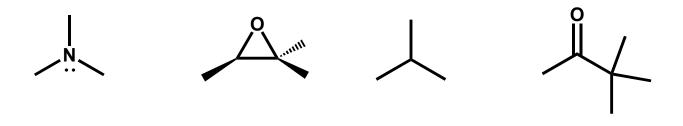
$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$$

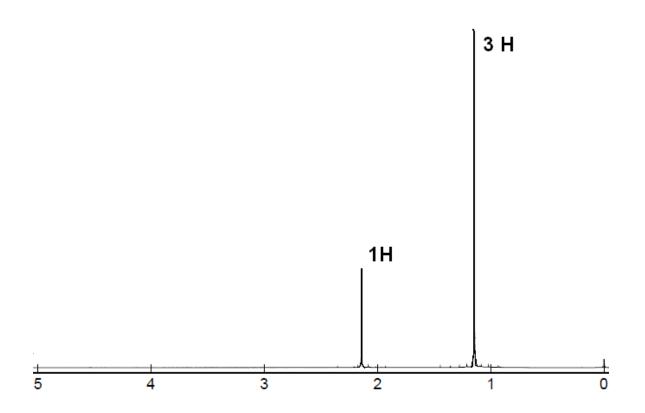
C.

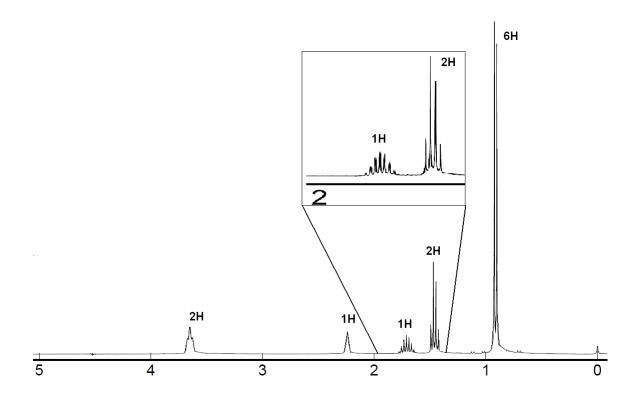


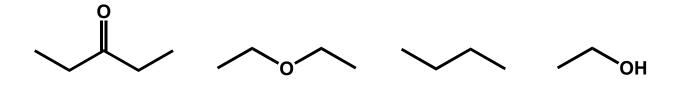
 $\textbf{D.} \hspace{1cm} (3S, 4S) \textbf{-3-Chloro-4-methylhex}$ 

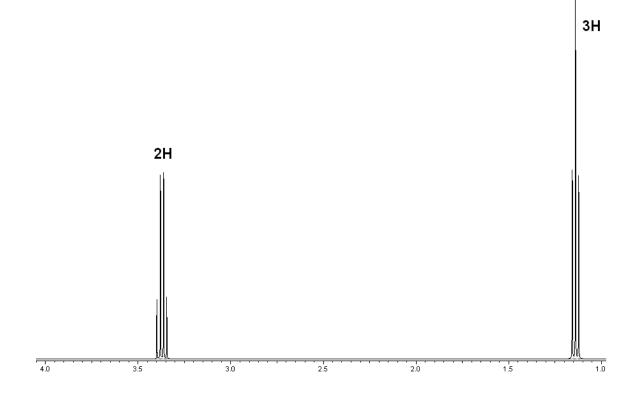


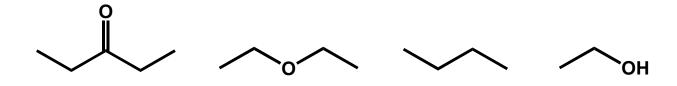


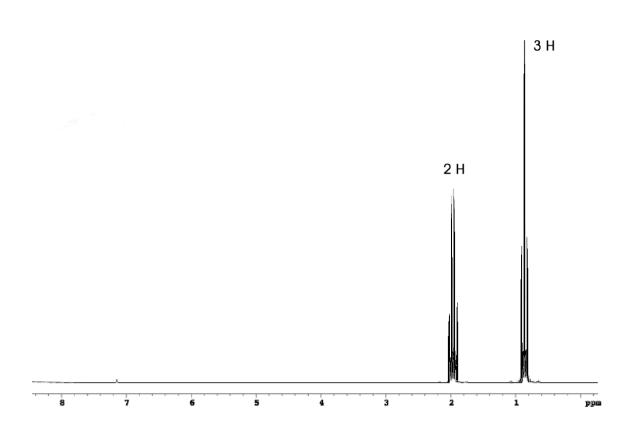


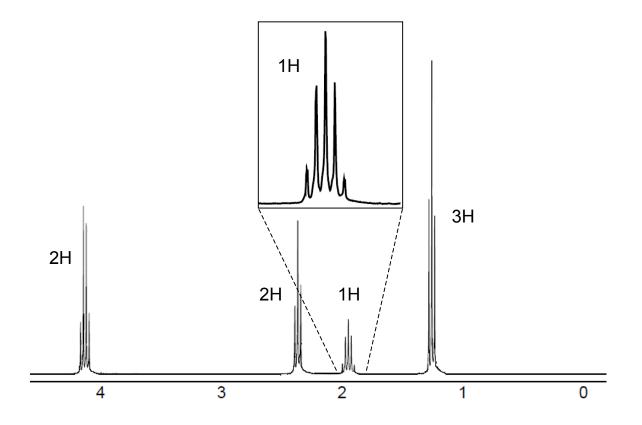




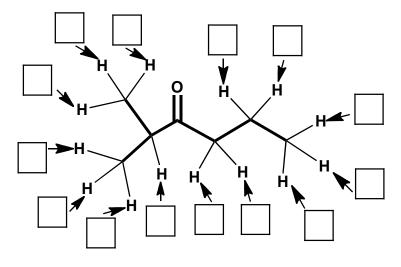


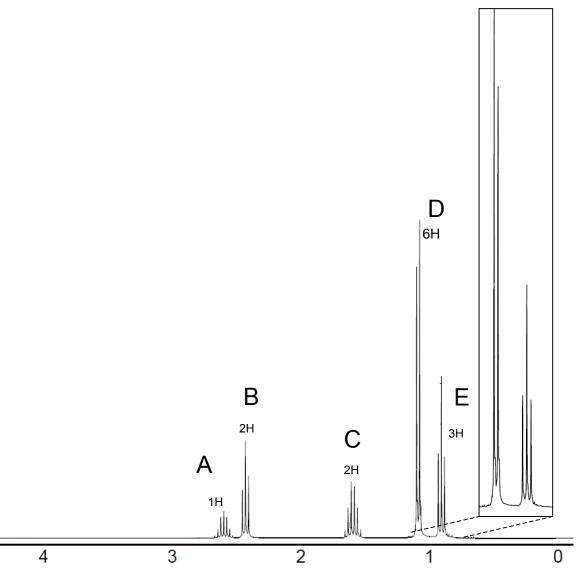






**5.** (14 pts) In the boxes provided, place that letter (A, B, C, etc.) that corresponds to the signals in the spectrum provided below.

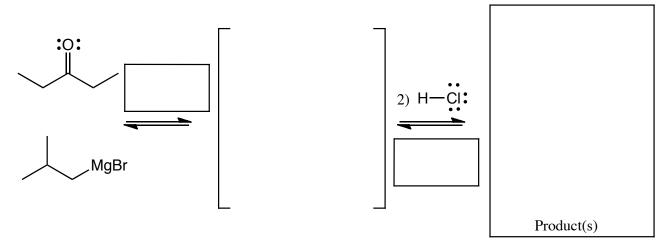




**6.** (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.

**7.** (6 pts) It is important to remember that organometallic reagents are bases as well as nucleophiles. These are important considerations when choosing a solvent. From the following list of common solvents, circle any that would be compatible with using an organolithium reagent.

8. (12 pts. total) Complete the mechanism for the following Grignard 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, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT. I realize these directions are complex, so please read them again to make sure you know what we want.



2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

Si	gna	ture						

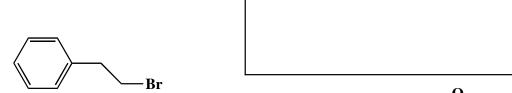
Pg 12 (18)

9. (cont.) (18 pts. total) Complete the mechanism for the following Wittig 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, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT. I realize these directions are complex, so please read them again to make sure you know what we want.

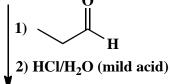
2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

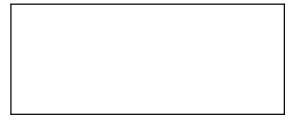


10. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get full credit, you only need to write the major organic product for these. You do not have to worry about the other products.

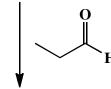


1) P(Ph)<sub>3</sub>
2) n-BuLi











10. (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. 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.



12. (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 You do not have to worry about the other products.

2) HCl/H<sub>2</sub>O (strong acid with some heat)

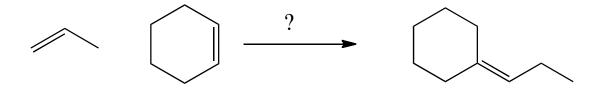
racemic

13. 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. 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. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

(10 pts) All of the carbon atoms of the products must come from the starting materials for this one!

13. 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. 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. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

(15 pts) All of the carbon atoms of the products must come from the starting materials for this one!



13. 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. 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. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

(13 pts) All of the carbon atoms of the products must come from the starting materials for this one!

14. (28 pts. total) This is a challenging problem so save it until the end. Complete the mechanism for the following 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. YOU HAVE NEVER SEEN THIS BEFORE, BUT WORK THROUGH IT USING THE PATTERNS YOU HAVE SEEN IN CLASS. IN OTHER WORDS, THIS REACTION FOLLOWS ALMOST THE EXACT PATTERN OF STEPS FOR A REACTION YOU HAVE SEEN.

Hint: this first intermediate is stabilized by resonance delocalization

$$\begin{array}{c|c} & & & \\ & & &$$