$\qquad$ Chemistry 310M/318M
Dr. Brent Iverson and Midterm
October 27, 2011

Please print the first three letters of your last name in the three boxes


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 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. PUT IT AWAY AND LEAVE IT THERE!!!

## 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.


Compound

| Hydrochloric acid | $\underline{\mathrm{H}}$-Cl | -7 |
| :---: | :---: | :---: |
| Protonated alcohol | $\mathrm{RCH}_{2}{ }^{\oplus}{ }_{\mathrm{O}}^{\mathrm{H}} \mathrm{H}_{2}$ | -2 |
| Hydronium ion | $\mathrm{H}_{3} \mathrm{O}^{\oplus}$ | -1.7 |
| Acetic acid |  | 4.8 |
| Ammonium ion | $\mathrm{H}_{4} \mathrm{~N}^{\oplus}$ | 9.2 |
| $\beta$-Dicarbonyls |  | 10 |
| Ethyl ammonium ion | $\mathrm{H}_{3} \mathrm{~N} \stackrel{\oplus}{-} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | 10.8 |
| $\beta$-Ketoesters |  | 11 |
| $\beta$-Diesters |  | 13 |
| Water | HOH | 15.7 |
| Alcohols | $\mathrm{RCH}_{2} \mathrm{OH}$ | 15-19 |
| Acid chlorides |  | 16 |
| Aldehydes |  | 18-20 |
| Ketones |  | 18-20 |
| Esters |  | 23-25 |

Terminal alkynes
$\mathrm{RC} \equiv \mathrm{C}-\underline{\mathrm{H}}$
25

LDA
$\underline{H}-\mathrm{N}\left(i-\mathrm{C}_{3} \mathrm{H}_{7}\right)_{2}$
40

Terminal alkenes
44

Alkanes
$\mathrm{CH}_{3} \mathrm{CH}_{2}-\mathrm{H}$
51

## PERIODIC TABLE OF THE ELEMENTS


$\qquad$ Pg 1 $\qquad$

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

## Where are the electrons?

2. ( 5 pts ) Draw the structures that corresponds to the following names:

## (5S,3E,6E)-5-ethyl-3,4-dimethyl-1,3,6-octatriene


3. (5 pts) Write an acceptable IUPAC name for the following molecule. Where appropriate, use E and $Z$ or $R$ and $S$.

(3S,4R,5S)-3,4,5-trimethyl-1,6-nonadiyne
4. ( 2 pts each no partial credit) The following statements are true. Choose from among the following three possibilities and in the space provided, write the letter of the one or more phenomena that explain the true statement.
A. The inductive effect
B. Hyperconjugation
C. Resonance delocalization of a charged species

is a stronger acid than

$\qquad$



is a more stable carbocation than
 because of: $\qquad$
5. ( 3 pts each) The following statements describe some important properties of molecules. Choose from among the following three types of isomers and in the space provided write the letter of the one or more types of isomers for which the statement is TRUE.
A. A pair of enantiomers
B. A pair of diastereomers
C. A pair of constitutional isomers

They might have different melting points. B, C
They might have different boiling points. B, C

They might taste differently. A, B, C

Assuming they are placed in the same solvent at the same concentration, the two solutions must rotate the plane of plane polarized light to an equal extent, but in opposite directions.


They might have different drug actions when injected into an animal or person. $\mathbf{A}, \mathbf{B}, \mathrm{C}$
6. (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, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing strucures. You might want to read these directions again to make sure you know what we want


7. For the following carbocation:
A) State the hybridization state of the indicated atom in the square box provided. In the rectangular boxes, describe the bonds indicated by the arrows in terms of overlap between hybrid orbitals (the valence bond approach). For example, answers might be $\boldsymbol{\sigma}_{\mathbf{C s p}}{ }^{3}-\mathbf{C s p}^{3}$ or $\boldsymbol{\pi}_{\mathbf{C} 2 p-C 2 p}$.
Note that this part of the question is NOT about hyperconjugation. We just want a valence bond description of the bonding in a carbocation structure.

B) ( 6 pts) This part refers to hyperconjugation. On the structure, circle all of the sigma bonds that can take part in hyperconjugation with the carbocation.
8. A) (8 pts) Complete the following structure of the artificial sweetener Nutrasweet ${ }^{\mathrm{TM}}$ at $\mathbf{p H} 3.0$, the pH of soft drinks like Diet Coke ${ }^{\mathrm{TM}}$. By adding appropriate numbers of lone pair electrons, $H$ atoms, and formal charges to the atoms in the boxes. (You do not have to add anything such as H atoms to atoms not drawn in the boxes.) This problem is testing your understanding of the relationship of protonation state to pH to pKa values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on each structure at the indicated pH . For your reference, here are the relavant $\mathrm{pK}_{\mathrm{a}}$ values:

B) (1 pt. each) On the above structure, put an asterisk next to each chiral center.
C) (2 pt) Given the number of chiral centers you identified, how many total stereoisomers are theoretically possible for Nutrasweet ${ }^{\mathrm{TM}}$ ?

$$
2^{2}=4
$$

D) (2 pt) What is the configuration at all the chiral centers in the molecule, R or S ?

S
E) (2 pt) Would you expect its enantiomer to taste the same as Nutrasweet ${ }^{\mathrm{TM}}$ ?
$\square$
F) ( 2 pt ) Would you expect its diastereomer to taste the same as Nutrasweet ${ }^{\mathrm{TM}}$ ?

No
G) $(2 \mathrm{pt})$ At pH of 7.0 , what is the total charge on the Nutrasweet ${ }^{\mathrm{TM}}$ molecule?

0
H) $(2 \mathrm{pt})$ At pH of 8.0 , what is the total charge on the Nutrasweet ${ }^{\mathrm{TM}}$ molecule?
$\qquad$ Pg 5
9. ( 8 pts ) For each acid-base reaction, circle the side of the equation that predominates at equilibrium. In each case identify the stronger and weaker acids by comparing relative stabilities of the anions which are the conjugate bases of the two acids.
Equilibrium favors formation of the weaker acid. You will notice this means you circled the side with the more stable anion.


10. (2 pts each) Write the four most common mechanism elements seen in organic chemistry reaction mechanisms.

1. Make a bond between a nucleophile and an electrophile
2. Break a bond to give stable molecules or ions
3. Add a proton
4. Take a proton away
(1 pt each) Fill in the blank with the single word that best completes the sentence
In reaction mechanisms, arrows indicate the movement of $\qquad$ ,
not $\qquad$ or charges. In the reactions of alkenes, the $\qquad$ pi
bond acts as a $\qquad$ nucleophile and reacts with a variety of electrophiles. The only reaction intermediates we have seen that rearrange are $\qquad$ _.

Pg 6 $\qquad$
11. (6 pts each) For each set of reagents, draw the first important intermediate or transition state that we discussed in lecture in the box provided. You must show all lone pairs and formal charges on the structures you draw!! Draw all species produced in this step of the mechanism Next, draw arrows on the starting materials to indicate electron flow to generate the intermediate or transition state that you have drawn. If the intermediate or transition state is chiral, you only need to draw one of the enantiomers, not both. Please read these directions again to make sure you know what we want. Note that we are only interested in the first step of the mechanism here, not the whole mechanism!

B.


Intermediate
D. For this one used dotted lines ( $\bullet \bullet \bullet \bullet$ ) to indicate bonds being made or broken in the structure you draw.


Signature $\qquad$ Pg. 7 $\qquad$
12. (28 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the reaction of an alkene with bromine in water, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or Take a proton away". MAKE SURE TO NOTICE THE QUESTIONS AT THE BOTTOM. Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is chiral, you only need to draw one enantiomer for this problem (we are making this easier for you).



(4 pts) During the reaction described by the above mechanism, say what happens to the pH of the
solution The pH would drop because acid is produced in the last step
( 4 pts ) Two of the above steps involves making a bond between a nucleophile and electrophile. Draw a circle areound the Nuclophile in these steps.
$\qquad$ $\operatorname{Pg} 8$ $\qquad$
13. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.
A.

$\square$
B.


$\square$
C.

$\square$
D.


1) $\mathrm{BH}_{3}$


E.



Raemic mixture
$\qquad$ Pg 9 $\qquad$
13 (cont.) (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.
F.





Racemic mixture
G.



H.





Racemic mixture
I.



(not chiral)
$\qquad$ Pg 10 $\qquad$ (17)

13 (cont.) ( 3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.
J.

$\qquad$
K.


L.


M.


N.


2.




Racemic mixture






$\qquad$
13 (cont.) ( 6 or 8 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.
0.


P.




Racemic mixture
$\qquad$ Pg 12 $\qquad$ (17)
14. ( 3,4 or 5 pts each) The following problems are a different format. In the space provided show the starting material, reagents or products to complete the scheme. If a pair of enantiomers are created, you must draw both and write "racemic" if appropriate.





14. ( 3,4 or 5 pts each) The following problems are a different format. In the space provided show the starting material, reagents or products to complete the scheme. If a pair of enantiomers are created, you must draw both and write "racemic" if appropriate.




(rearranged)


$\mathrm{H}_{2}$
Lindlar's catalyst

15. Here is an "apply what you know" problem in the format of an MCAT style passage. Circle the correct answers.

Carbocations are intermediates in several of the reactions we have seen this semester. In addition, it is possible to make carbocations from functional groups other than alkenes, such as alcohols and haloalkanes. In the reactions we have seen, carbocations act as strong electrophiles, making new bonds with nucleophiles. In addition, we have seen another reaction of carbocations in which an H atom, or more rarely an alkyl group, migrates to generate a more stable carbocation. This carbocation rearrangement process is sometimes referred to as a 1,2 shift to indicate that an H atom or alkyl group has moved to the adjacent carbocation center. As stated in class, a carbocation rearrangement can be thought of as being related to hyperconjugation in the sense that the process begins through donation of sigma bonding electron density from the group that will move into an empty 2 p orbital on the C atom with a positive charge.

It turns out that carbocations can undergo another characteristic reaction in which a proton is lost.


Losing a proton from a carbocation gives an alkene. Next week, we are going to refer to this sequence of steps as an E1 reaction; formation of a carbocation followed by loss of a proton. Several well-known reactions involve carbocation formation, followed by loss of a proton to give a new pi bond.

1. The process shown above, in which a proton is taken away from a carbocation to form an alkene, is in many ways the functional reverse of the first step in which mechanisms:
A. Addition of H Br to an alkene
B. Addition of $\mathrm{Br}_{2}$ to an alkene
C. Addition of $\mathrm{H}_{2} \mathrm{O}$ to an alkene in the presense of a catalytic amount of $\mathrm{H}_{2} \mathrm{SO}_{4}$
D. Both A. and C.
$\qquad$

## 15 (cont.).

2. (4 pts) The following four carbocations have numbers underneath them. Select the letter that lists the carbocations in order of stability, with the first being the MOST stable and the last being the LEAST stable.


1


2


3


4
A. $1,2,3,4$
B. $4,3,2,1$
C. $3,2,1,4$
D. $4,1,2,3$
3. (4 pts) The following three reactions are run in the laboratory. Indicate which one(s) are expected to show a significant amount of rearranged products.



A. 1
B. 2,3
C. 1,2
D. $1,2,3$
4. (4 pts) The following three reactions are run in the laboratory. Indicate which one(s) are expected to show a significant amount of rearranged products.



A. 1
B. 2,3
C. 1,3
D. $1,2,3$

## 15 (cont.).

5. (4 pts) The following carbocation might be expected to give a significant amount of rearrangement under the correct experimental conditions. Select the letter that accurately describes which rearranged product might be seen.



1


2


3
A. 1
B. 2
C. 3
D. Rearrangement is not possible for this carbocation
6. As mentioned in the passage, carbocations can lose a proton and create a double bond under certain conditions. It is commonly observed that the most stable of any possible alkenes form under these conditions. The following carbocation is created in conditions suitable to favor rearrangement then loss of a proton to form an alkene. Which alkene will be formed as the predominant alkene product under these conditions?

A. 1
B. 2
C. 3
D. 4

