

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
2nd Midterm
October 25, 2012

SIGNATURE: _____

**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 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!!!

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)

| Page | Points |
|--------------|--------------|
| 1 | (15) |
| 2 | (24) |
| 3 | (22) |
| 4 | (28) |
| 5 | (16) |
| 6 | (12) |
| 7 | (22) |
| 8 | (25) |
| 9 | (11) |
| 10 | (14) |
| 11 | (13) |
| 12 | (18) |
| 13 | (8) |
| 14 | (12) |
| Total | (240) |

| Compound | | pK _a |
|--------------------|-----------------------------------------------------------------------------------------------------------------|-----------------|
| Hydrochloric acid | H-Cl | -7 |
| Protonated alcohol | $\text{RCH}_2\text{O}^+\text{H}_2$ | -2 |
| Hydronium ion | H_3O^+ | -1.7 |
| Acetic acid | $\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{H}$ | 4.8 |
| Ammonium ion | H_4N^+ | 9.2 |
| β-Dicarbonyls | $\text{RC}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CR}'$ | 10 |
| Ethyl ammonium ion | $\text{H}_3\text{N}^+-\text{CH}_2\text{CH}_3$ | 10.8 |
| β-Ketoesters | $\text{RC}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'$ | 11 |
| β-Diesters | $\text{ROC}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'$ | 13 |
| Water | HOH | 15.7 |
| Alcohols | RCH_2OH | 15-19 |
| Acid chlorides | $\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$ | 16 |
| Aldehydes | $\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H}$ | 18-20 |
| Ketones | $\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{R}'$ | 18-20 |
| Esters | $\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'$ | 23-25 |
| Terminal alkynes | $\text{RC}\equiv\text{C}-\text{H}$ | 25 |
| LDA | $\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$ | 40 |
| Terminal alkenes | $\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$ | 44 |
| Alkanes | $\text{CH}_3\text{CH}_2-\text{H}$ | 51 |

PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

| | Electron | Proton | Neutron | Positron | Neutrino |
|-----------------------------|-------------------------------|--------------------------------|---------------------------------|----------|----------|
| Symbol | e | p | n | γ | ν |
| Rest mass (kg) | $9.109389(5) \times 10^{-31}$ | $1.672623(1) \times 10^{-27}$ | $1.674929(2) \times 10^{-27}$ | 0 | 0 |
| Relative atomic mass | $5.485799(9) \times 10^{-4}$ | $1.00727647(1) \times 10^{-3}$ | $1.008664916(8) \times 10^{-3}$ | 0 | 0 |
| Positive charge (e) | -1 | 1 | 0 | 1 | 0 |
| Spin | $1/2$ | $1/2$ | $1/2$ | $1/2$ | $1/2$ |

% Ionic Character of a Single Chemical Bond

| Difference in Electronegativity | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 | 2.0 | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | 2.6 | 2.7 | 2.8 | 2.9 | 3.0 |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| % Ionic Character (Pauling) | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 | 2.0 | 2.2 | 2.4 | 2.6 | 2.8 | 3.0 | 3.2 | 3.4 | 3.6 | 3.8 | 4.0 | 4.2 | 4.4 | 4.6 | 4.8 | 5.0 | 5.2 | 5.4 | 5.6 | 5.8 | 6.0 |
| % Ionic Character (Huggins) | 1.6 | 2.3 | 3.1 | 3.9 | 4.7 | 5.5 | 6.3 | 7.1 | 7.9 | 8.7 | 9.5 | 10.3 | 11.1 | 11.9 | 12.7 | 13.5 | 14.3 | 15.1 | 15.9 | 16.7 | 17.5 | 18.3 | 19.1 | 19.9 | 20.7 | 21.5 | 22.3 | 23.1 | 23.9 | 24.7 |

1 IA

2 IIA

3 IIIA

4 IVA

5 VA

6 VIA

7 VIIA

8 VIIIA

9 VIIIA

10 VIIIA

11 IB

12 IIB

13 IIIA

14 IVA

15 VA

16 VIA

17 VIIA

18 VIII

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | |
|----------|--------|----------|-------------|-------------|------------|-------------|------------|----------|----------|--------|-----------|----------|---------|------------|--------|----------|-------|-----------|---------|----------|----------|----------|----------|-----------|------|--------|--------|--------|------|---------|-----------|---------|----------|---------|---------|--|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | |
| H | He | Li | Be | B | C | N | O | F | Ne | Na | Mg | Al | Si | P | S | Cl | Ar | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Hydrogen | Helium | Lithium | Beryllium | Boron | Carbon | Nitrogen | Oxygen | Fluorine | Neon | Sodium | Magnesium | Aluminum | Silicon | Phosphorus | Sulfur | Chlorine | Argon | Potassium | Calcium | Scandium | Titanium | Vanadium | Chromium | Manganese | Iron | Cobalt | Nickel | Copper | Zinc | Gallium | Germanium | Arsenic | Selenium | Bromine | Krypton | |
| 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 120 | 121 | 122 | 123 | 124 | 125 | 126 | 127 | 128 | 129 | 130 | 131 | 132 | 133 | 134 | 135 | 136 | |
| Fr | Ra | Ac | Unq | Unp | Unh | Uns | Uno | Uue | Uun | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Francium | Radium | Actinium | Unquadecium | Unpentacium | Unhexacium | Unseptacium | Unoctacium | Unennium | Unbinium | | | | | | | | | | | | | | | | | | | | | | | | | | | |

Elementary Subatomic Particles

Electron, Proton, Neutron, Positron, Neutrino

Rest mass (kg), Relative atomic mass, Positive charge (e), Spin

% Ionic Character of a Single Chemical Bond

Difference in Electronegativity, % Ionic Character (Pauling), % Ionic Character (Huggins)

Pauling's electronegativity values are based on the relative ability of an atom to attract electrons to itself in a molecule.

25

Mn

Manganese

Atomic Weight, Melting Point, Boiling Point, Density, Electronegativity, First Ionization Potential

| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
|---------|--------------|-----------|------------|-----------|-----------|------------|-----------|-------------|-------------|---------|-------------|-----------|------------|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 140.12 | 140.907 | 144.24 | | 150.36 | 151.965 | 157.25 | 158.9254 | 162.50 | 164.93032 | 167.259 | 168.93421 | 173.04 | 174.967 |
| Cerium | Praseodymium | Neodymium | Promethium | Samarium | Europium | Gadolinium | Terbium | Dysprosium | Holmium | Erbium | Thulium | Ytterbium | Lutetium |
| 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 120 | 121 | 122 | 123 |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| Thorium | Protactinium | Uranium | Neptunium | Plutonium | Americium | Curium | Berkelium | Californium | Einsteinium | Fermium | Mendelevium | Nobelium | Lawrencium |

PAPERTECH

Editors: T. K. Yarg, M.A.Sc. & C. Bello, M.A.Sc.

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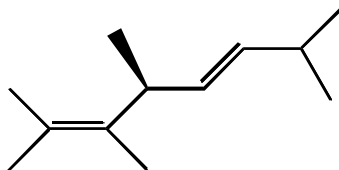
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Signature _____

Pg 1 _____(15)

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

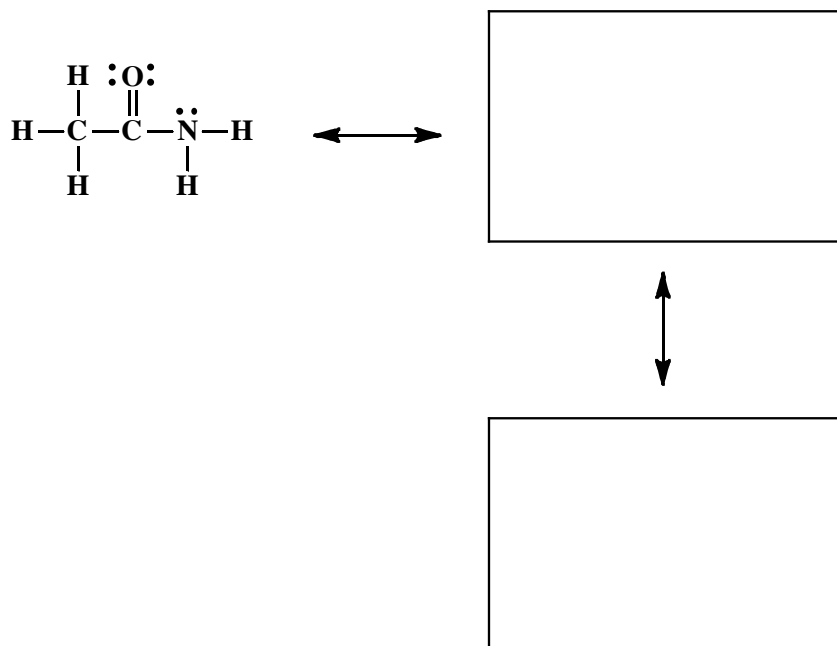
2. (5 pts) Write an acceptable IUPAC name for the following two molecules. Where appropriate, use E and Z or R and S.



3. (5 pts) Draw the structure that corresponds to the following name:

(3E,5Z,7Z)-1,3,5,7,10-undecapentaene

4. (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 structures. You might want to read these directions again to make sure you know what we want

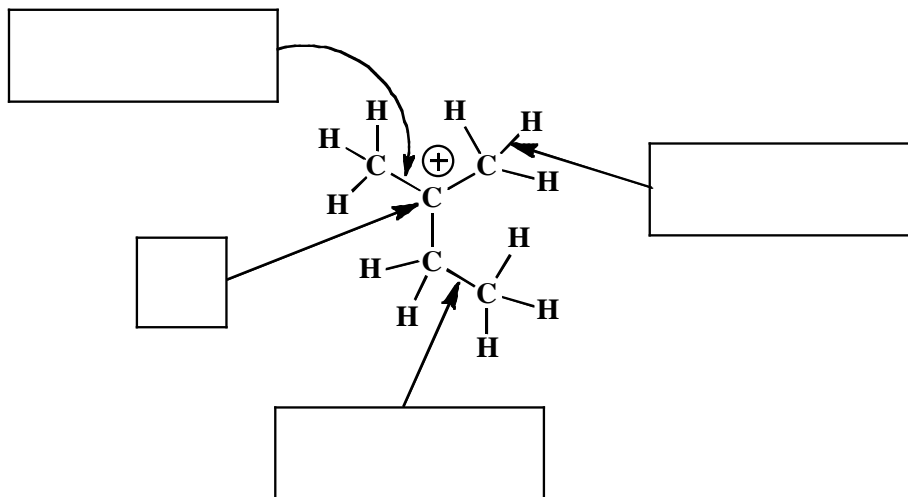


5. For the following carbocation:

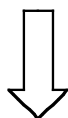
A) State the hybridization state of the indicated atom in the square box provided. In the rectangular boxes, describe the bonds indicated by the arrows in terms of overlap between hybrid orbitals (the valence bond approach). For example, answers might be $\sigma\text{Csp}^3\text{-Csp}^3$ or $\pi\text{C}2\text{p-C}2\text{p}$.

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.

(2 pts. each)

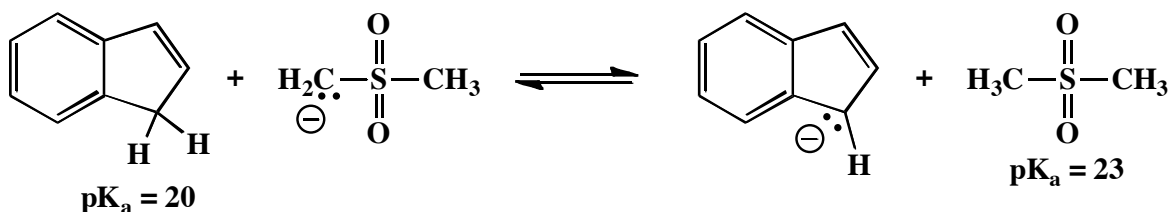
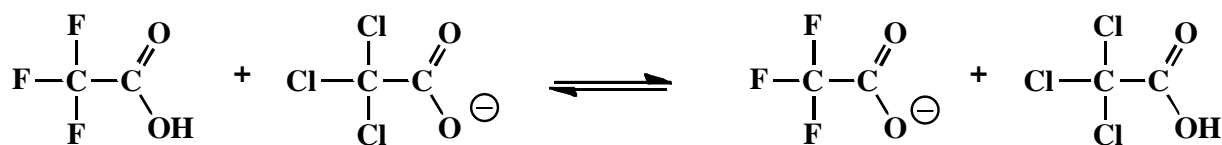
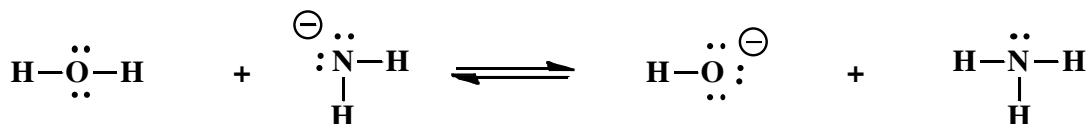


NOTICE THIS



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.**

6. (6 pts) For each acid-base reaction, **circle the side of the equation that predominates at equilibrium.**



7. (2 or 4 pts each) For the following, **circle the capitalized word** that best completes the statement.

In general, it is best to think of alkenes and alkynes as **NUCLEOPHILES** or **ELECTROPHILES** that react with **NUCLEOPHILES** or **ELECTROPHILES**.

In general, **NUCLEOPHILES** or **ELECTROPHILES** serve as electron sources and **NUCLEOPHILES** or **ELECTROPHILES** serve as electron sinks for most reactions.

A pi bond or lone pair will serve as an **ELECTRON SOURCE** or **ELECTRON SINK** for an arrow that indicates the making of a new bond.

An atom that can accommodate a new bond can serve as an **ELECTRON SOURCE** or **ELECTRON SINK** for an arrow that indicates the making of a new bond.

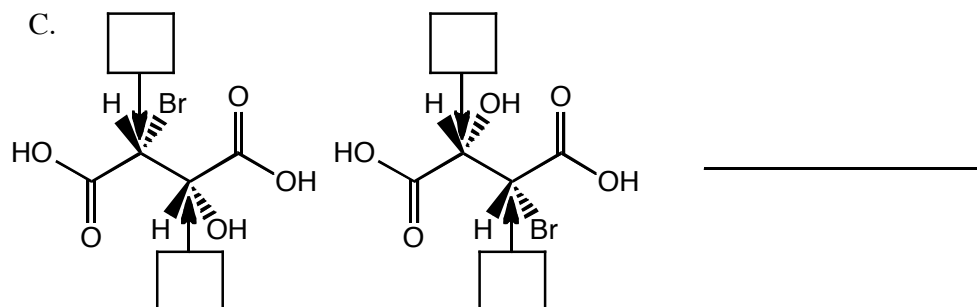
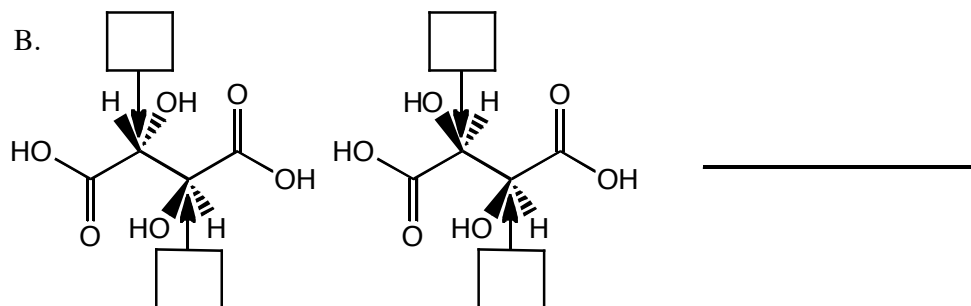
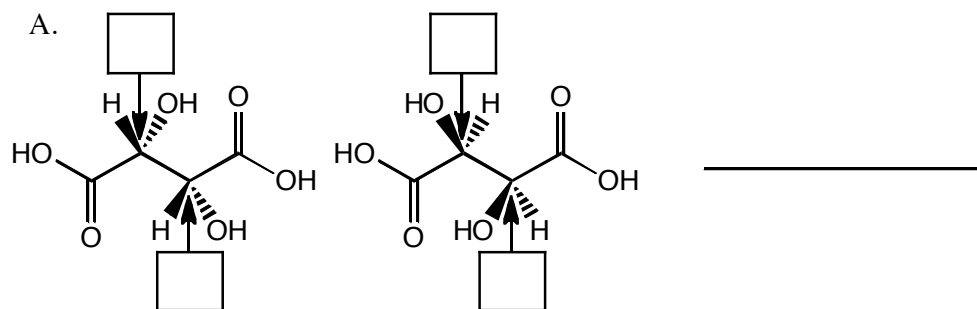
A reaction that occurs faster (greater opportunity) has a **LOWER** or **HIGHER** activation energy.

A reaction that has a strong thermodynamic driving force (a strong motive) is **FAVORABLE** or **UNFAVORABLE** as written.

8. (2 pts each) Write the four most common mechanism elements seen in organic chemistry reaction mechanisms.

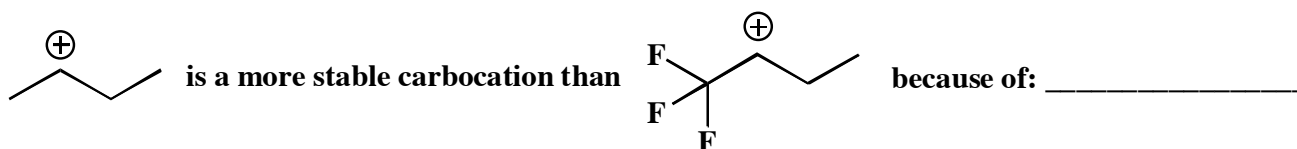
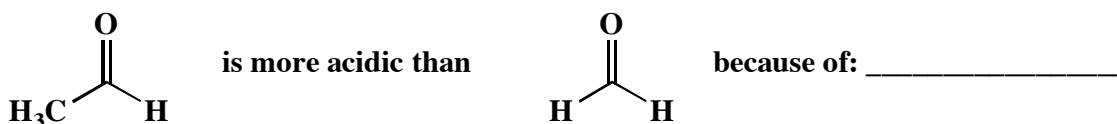
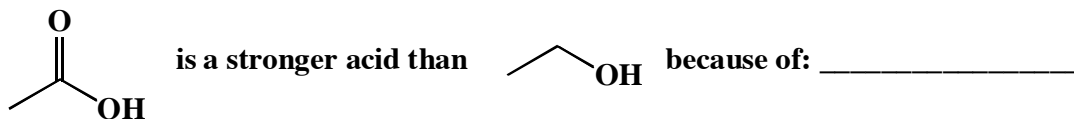
9. (6 or 8 pts each) Label each stereocenter as "R" or "S" and on the line provided state whether the pair of molecules represent two enantiomers, two diastereomers, or the same compound.

Draw a circle around any meso compound.



10. (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 best explain the true statement.

A. The inductive effect B. Hyperconjugation C. Resonance delocalization of a charged species



11. (2 pts each no partial credit) 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 single enantiomer B. A meso compound C. A racemic mixture

A solution of this will rotate the plane of plane polarized light. _____

A solution of this will NOT rotate the plane of plane polarized light. _____

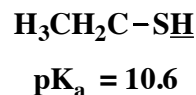
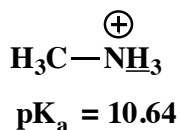
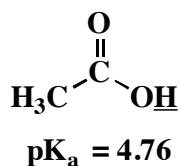
Might be produced when an alkene with no chiral centers reacts with a non-chiral reagent such as H-Br or Br₂. _____

The LEAST desirable option when developing a new drug _____

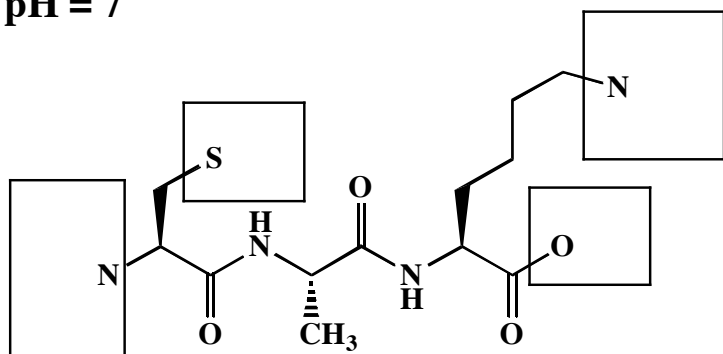
Signature _____

Pg 6 _____(12)

12. (12 pts) Complete the following two structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (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 pK_a 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 relevant pK_a values:

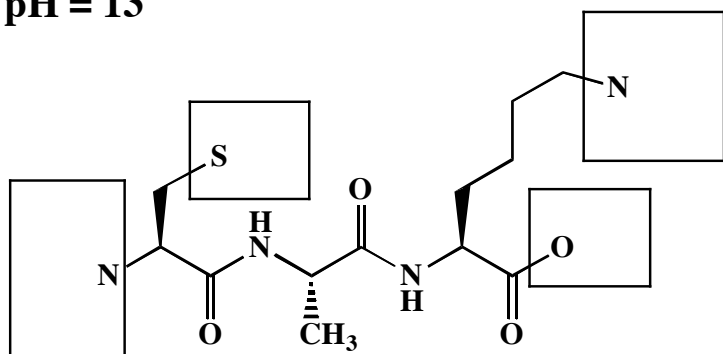


pH = 7



Total charge on molecule: _____

pH = 13

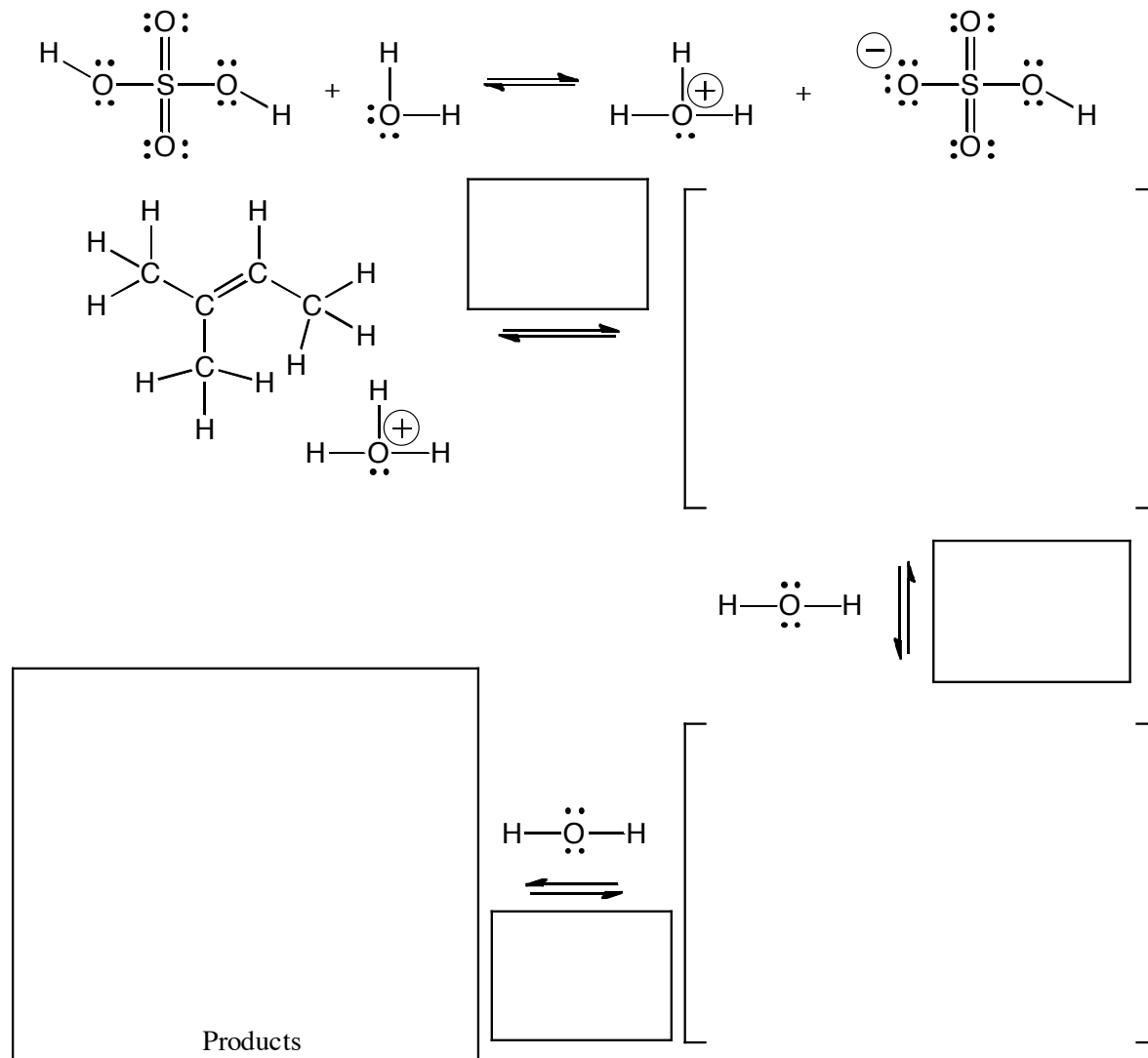


Total charge on molecule: _____

Signature _____

Pg. 7 _____ (22)

13. (16 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the reaction of an alkene with water and a small amount of sulfuric acid shown below, 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. If an intermediate or product is chiral, you only need to draw one enantiomer for this problem.

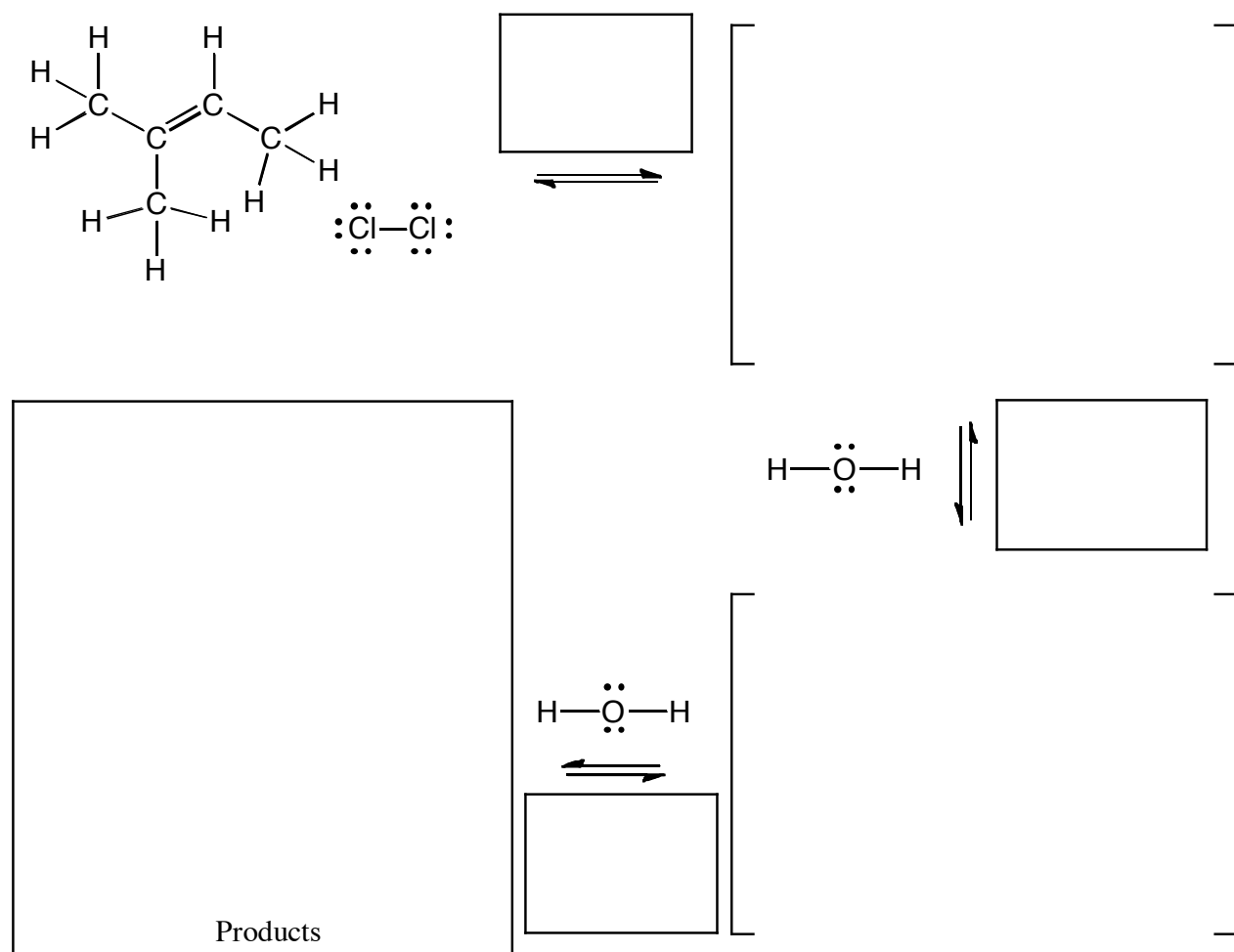


(2 pts) During the reaction described by the above mechanism, what happens to the pH of the solution _____

(2 pts) Is this reaction catalytic in acid? _____

(2 pts) One of the above steps involves making a bond between a nucleophile and an electrophile. Draw a circle around the electrophile.

14. (21 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the reaction of an alkene with water in the presence of Cl_2 shown below, 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. If an intermediate or product is chiral, you only need to draw one enantiomer for this problem. For the product, you must draw both enantiomers and write "racemic" if appropriate.



(2 pts) During the reaction described by the above mechanism, say what happens to the pH of the solution _____

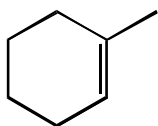
(2 pts) Is this reaction catalytic in acid? _____

Signature _____

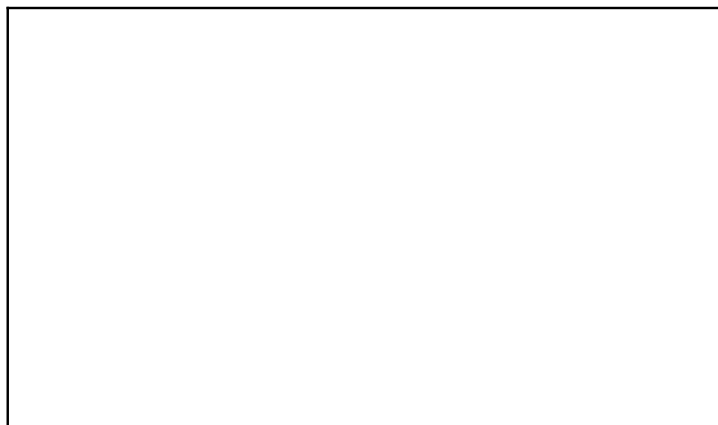
Pg 9 _____(11)

15. (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**.

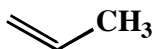
A.



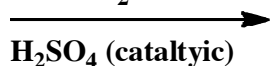
HBr



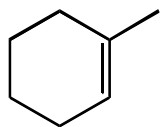
B.



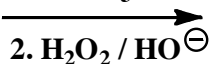
H₂O



C.

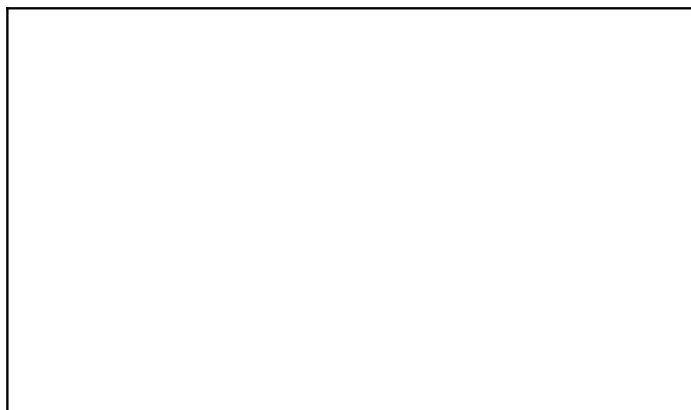
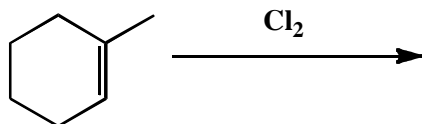


1. BH₃

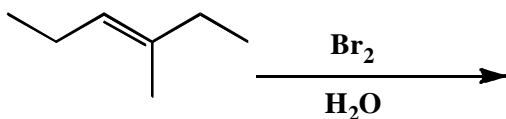


15. (cont.) (4 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember 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**.

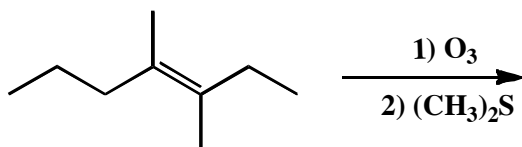
D.



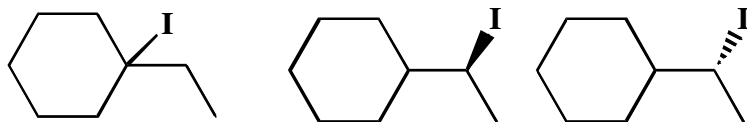
E.



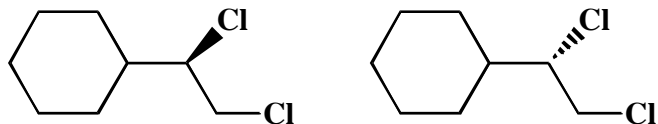
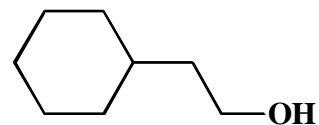
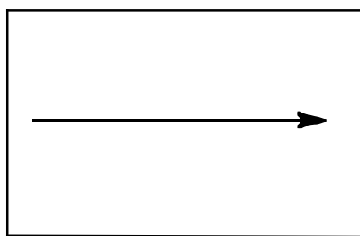
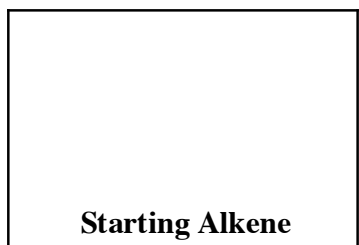
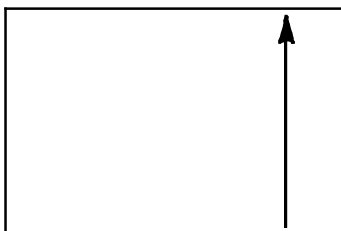
F.



16. (13 pts total) Organic chemistry is a very creative science because there are so many different reactions known that often we are only limited by our imaginations. For example, the same starting alkene can be converted to the different products listed. **Deduce the identity of the starting alkene, and write its structure in the box labeled "Starting Alkene".** Fill in the boxes containing arrows with the reagents required to produce the given products.



Racemic



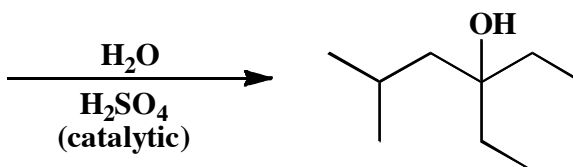
Racemic

17. (6 pts each) The following problems are a new format. We turn the tables and give you the product. In the space provided show the starting material required to make that product using the given reagents. When more than one starting material would work, you must draw both.

A.



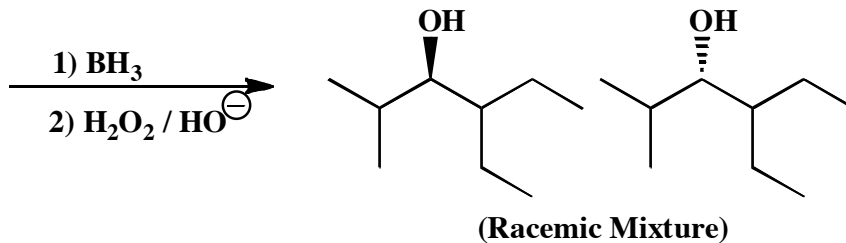
or



B.



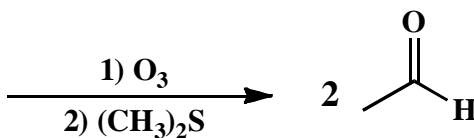
or



C.



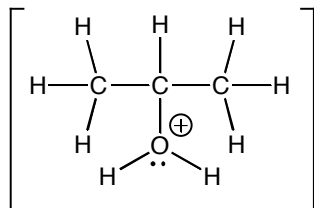
or



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

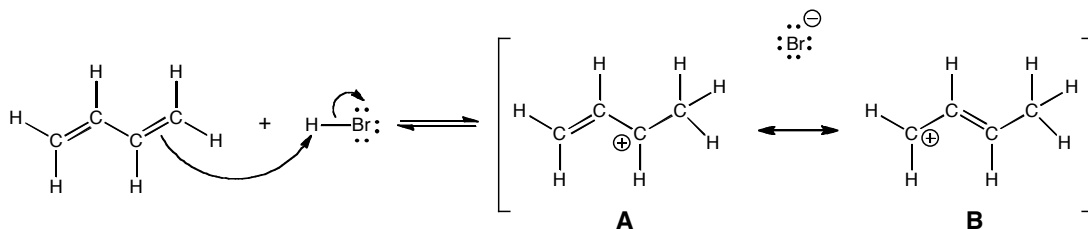
One of the more difficult things for new organic students to master is how to recognize an electrophile. One key piece of information is the charge you see on an atom. An atom with a full or partial positive charge is worth considering as an electrophile. However, not all atoms with a full or partial positive charge are electrophiles. To be an electrophile, an atom must be capable of acting as a "sink" for a mechanism arrow. In other words, it must be able to accept a new bond from a nucleophile. The best electrophile we have seen is a carbocation, capable of reaction with nucleophiles such as halide anions and water. As you continue your study of organic chemistry, you will encounter several other electrophiles. The following questions examine some of these. Although you have not seen all of them before, you are already familiar with all of the fundamental concepts you need to deduce the correct answers.

1. The following intermediate structure has a positive charge on the O atom.



- The O atom is an electrophile because a nucleophile can add to it without causing the breaking of any of the other bonds to O.
- The O atom is an electrophile because although it already has a filled valence, a proton (H^+) can depart as the new bond is made.
- The O atom is not an electrophile because hyperconjugation stabilizes it.
- The O atom is not an electrophile because it already has a filled valence and adding a new bond would require the creation of a very high energy species such as an H or C atom with a lone pair and thus negative charge.

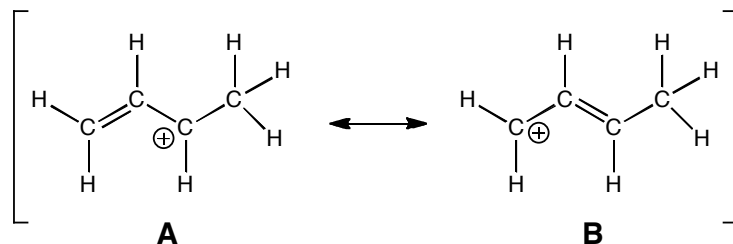
2. The following carbocation is encountered in a reaction you will study next semester.



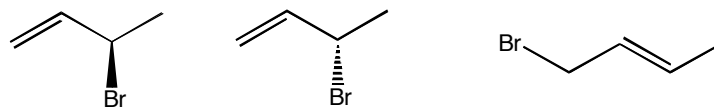
- The contributing structure A makes a larger contribution to the resonance hybrid.
- The contributing structure B makes a larger contribution to the resonance hybrid.
- The two contributing structures make equal contributions.
- There is a third contributing structure that is not shown even though it makes the major contribution to the resonance hybrid.

18. (cont.).

3. Here again is the same carbocation you saw in part 2.



- A. This carbocation is stabilized because it has a “pi-way”, that is a pi orbital that extends over more than two atoms.
- B. This carbocation is stabilized by delocalization of the positive charge over more than one atom.
- C. Both A and B.
- D. This carbocation is less stable than an analogous carbocation that does not have an adjacent pi bond.
4. If the carbocation shown in parts 2 and 3 reacted with the bromide anion, one could imagine at least three different products that could form.



- A. The product on the left is the only one that could form.
- B. The product on the right is the only one that could form.
- C. Only the product on the left and the product in the middle could form.
- D. All three products could form.
5. Of the three products shown in part 4, which one(s) would you expect to be the most stable
- A. The molecule on the left is the most stable
- B. The molecule on the right is the most stable
- C. The two molecules on the left have the same stability and they are both more stable than the molecule on the right.
- D. All three molecules have the same stability