Dr. Richter

PRINT NAME $\qquad$ .
SIGN NAME $\qquad$ .

You are required to answer all questions. Please write legibly and draw clearly. Points will be deducted for illegible and unclear answers. Please answer in the space provided near each question. Use the reverse side if you need more space. There are a total of 210 points possible for this exam and the value of each question is shown in parenthesis beside each question or section. READ ALL QUESTIONS CAREFULLY AND APPORTION YOUR TIME APPROPRIATELY.

## Part I: New Material (100 points total)

A. Structure/Mechanism/Reactivity. (46 pts total)

1. For parts $\mathbf{a}$ and $\mathbf{b}$, draw the alkene that would give the indicated products. Draw your answers in the provided boxes. (12)
a


2. The reaction below proceeds through a six-step mechanism (after proton transfer from sulfuric acid to water). The steps of the reaction are labeled below as A-F. These steps are not in the correct order and are missing some mechanistic arrows, reactants, and/or products. Your tasks are to i.complete each step by filling in all missing items and ii. place the steps in the correct sequential order (in the box provided at the top right of the page). You may use the last page as scratch paper. (19)

## Overall Reaction:



Order of Steps:

$$
\overline{1^{\text {st }}} \quad \overline{2^{\text {nd }}} \quad \overline{3^{\text {rd }}} \overline{4^{\mathrm{th}}} \overline{5^{\text {th }}} \overline{6^{\mathrm{th}}}
$$





E
 $\rightleftharpoons$
c


F

3. Indicate whether each statement a-e is true (T) or false (F). (15)
$\qquad$ a. A secondary alcohol can be oxidized to a carboxylic acid with $\mathrm{CrO}_{3} / \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$.
$\qquad$ b. The hydration of a triple bond always results in an aldehyde product.
$\qquad$ c. Oxidative cleavage of 1 mol of $\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}$ would yield 1 mol of an aldehyde and 1 mol of a ketone.
$\qquad$ d. The addition of HCl to an asymmetric alkene is an example of a process that follows Markovnikov's rule.
$\qquad$ e. The treatment of $\mathrm{CH}_{3} \mathrm{C} \equiv \mathrm{CCH}_{3}$ with excess $\mathrm{H}_{2}$ in the presence of $\mathrm{Pd}-\mathrm{C}$ will yield a mixture of diastereomers.

## B. Predict the Products. (54 pts total)

For each of the questions below (4-12) draw the major organic product(s), showing stereochemistry when appropriate. (6 pts each)
4.

5.

6.

7.

8.

9.

10.

11.



## Part II: Old Material (70 points total)

A. Structure/Mechanism/Reactivity. (34 pts total)

Consider structures a-e below then answer questions 13-15.

a

b

c

d

e
13. Which structure(s) a-e would be optically active? Circle all correct answers. (6)
a
b
c
d
e
14. Draw one diastereomer of structure e. (2)
15. Draw the enantiomer of structure b. (2)
a

(
d


。

c


16. List all reactions a-f that would proceed through a carbocation.
17. List all reactions a-f that would yield a chiral product.
18. List all reactions a-f that would yield an alkene as the major product.
19. The rate of reaction $\mathbf{b}$ would increase if $[\mathrm{KCN}]$ was increased.
True False
20. The rate of reaction e would increase if the alcohol were tertiary instead of secondary.

$$
\text { True } \quad \text { False }
$$

21. The rate of reaction $f$ would increase if the tosylate were tertiary instead of secondary. True False

Consider the structure below (erlotinib hydrochloride, a lung cancer drug marketed as Tarceva) and answer question 22.

22. For a-c circle your answers. (6)
a. One nitrogen atom in this compound is $\mathrm{sp}^{3}$-hybridized.

True False
b. At least one oxygen atom in this compound will have some $\mathrm{sp}^{2}$-character.

True False
c. If protons $\mathbf{A}, \mathbf{B}$, and $\mathbf{C}$ are listed in order of increasing pKa , the correct order is:
$B<C<A$
$C<B<A$
$B<A<C$
$\mathrm{A}<\mathrm{C}<\mathrm{B}$
$A<B<C$

Bonus Question: Why is the drug given in the form of a salt? (2 pts)

## B. Predict the Product(s) (20 pts total)

For each of the questions below (23-27), draw the major organic product(s), showing stereochemistry when appropriate. (4 pts each)
23.

24.

25.

26.

27.

C. Spectroscopy ( 16 pts total)
28. Match each structure A-D with an IR spectrum (1-4). Write your answers on the lines underneath the structures. (8)


A

Answers: $\qquad$

## IR Spectra:




29. Match each of the four structures (1-4) below with an proton NMR spectrum (a-d). Write your answers on the lines underneath the structures. (8)

1

2

3

4

## Answers:

$\qquad$





Part III: Synthesis. May use "Old" and "New" Material (40 pts total)
30. Propose a reasonable synthesis, starting from the indicated substrate in each case. You may use any inorganic reagents you deem necessary. You may also use any organic acids, bases, oxidizing, or reducing agents. (16 pts)

31. Complete the reaction scheme below by filling in the appropriate missing products and reactants. Place you answers in the provided table on the next page. (24)


ANSWERS:

| A |  |  |  |
| :--- | :--- | :--- | :--- |

SCRATCH PAPER
Put final answers on appropriate page. Answers on this page will NOT be graded.

