Hour Exam #1
Chemistry 345
Professor Gellman
19 February 2014

Last Name Answer Key

First Name

General Instructions:

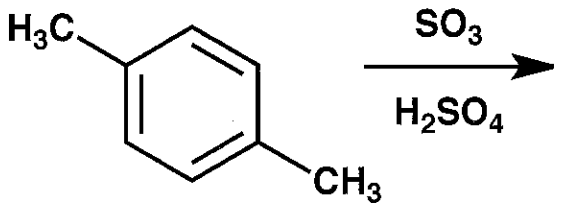
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

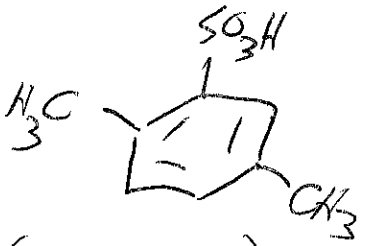
(ii) Print your name on each page.

(iii) Please keep your paper covered and your eyes on your own work. No electronic devices may be used. Misconduct will lead to failure in the course.

1. (17 points) Show the product(s) expected from the reactions indicated below.

(a)



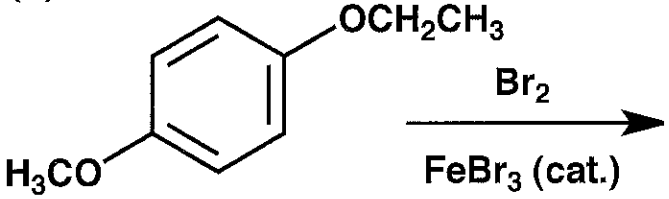



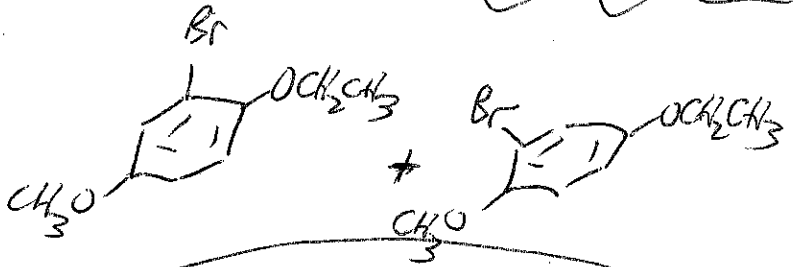

15

(-1 for $SO_3$
-2 for $SO_2$)

-1 for extra and/or incorrect structures

(b)

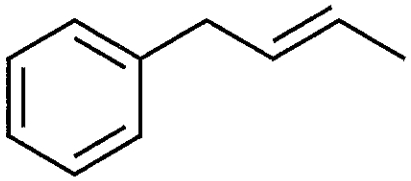



+5 for one; +7 for both

+2 for dibrominated product

(c)



H2
Pd/C
room temp

+5

Name _____

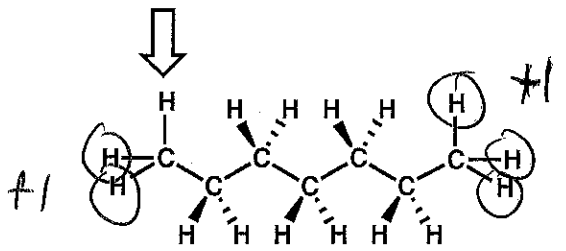
2. (15 points)

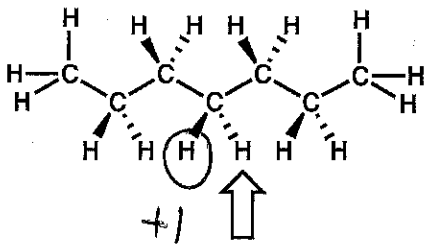
For each molecular drawing below, with reference to the H indicated by the arrow, label other H's as indicated...

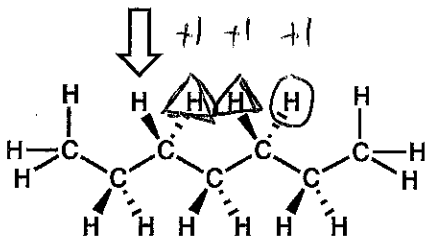
...Put a CIRCLE around any homotopic H's.

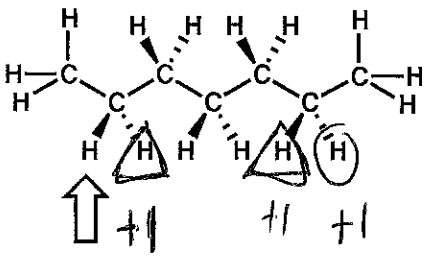
...Put a TRIANGLE around any enantiotopic H's.

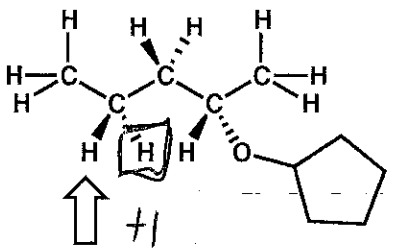
...Put a SQUARE around any diastereotopic H's.

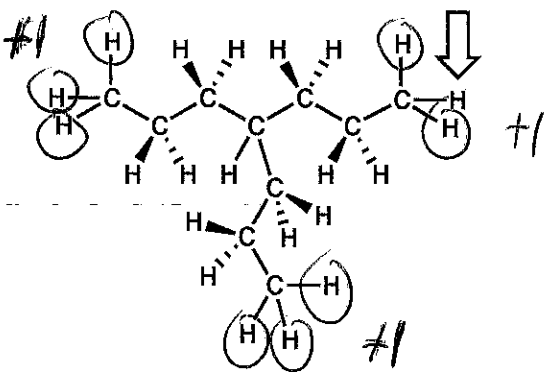


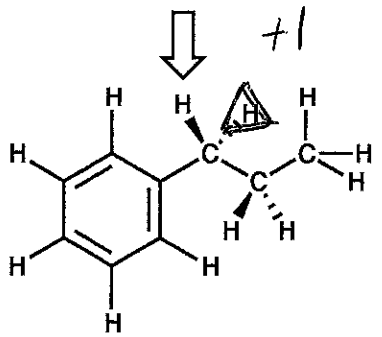


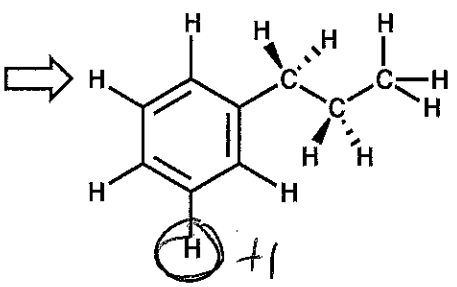






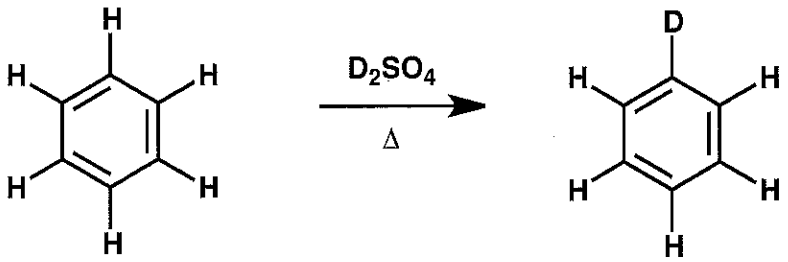




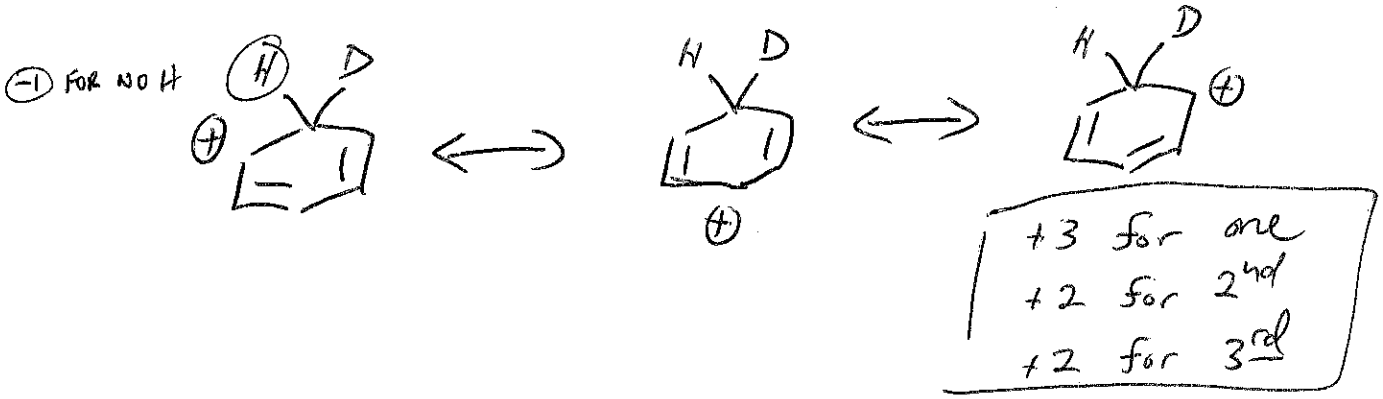


Name _____

3. (16 points) If benzene is heated with $D_2SO_4$ (D is deuterium), H atoms on the ring are slowly replaced with D. Shown below is the result of a single replacement.

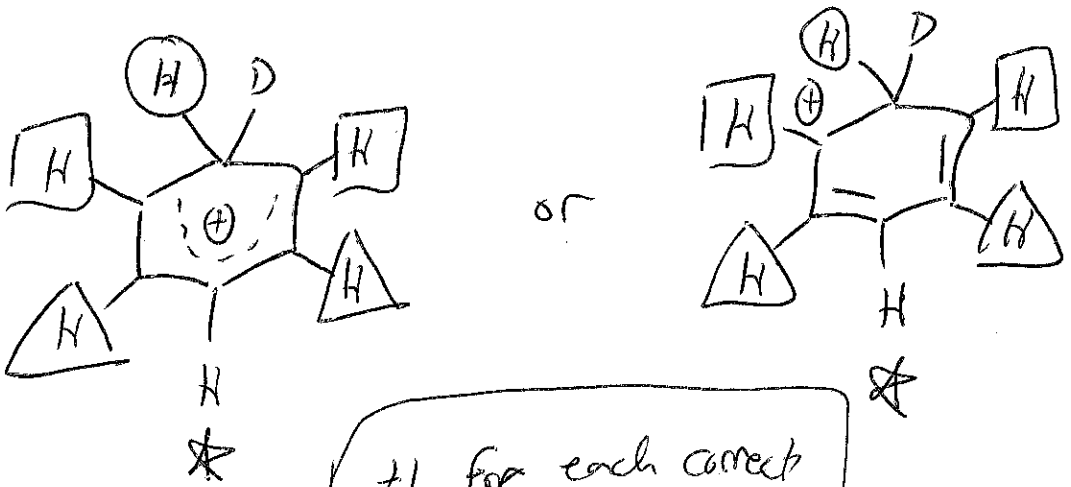



(a) This reaction is an example of electrophilic aromatic substitution. Draw the cationic intermediate for formation of the mono-deuterated product shown above (all resonance structures).




(b) Under special conditions, this intermediate is stable enough that a proton NMR spectrum can be obtained. Below, indicate in the box how many types of H resonances you expect for this intermediate (don't worry about splitting). In the space below the box, provide a drawing of this intermediate in which all H's are shown and for which you indicate each set of magnetically equivalent H's with a distinct symbol (circles, squares, triangles, crosses, etc.).

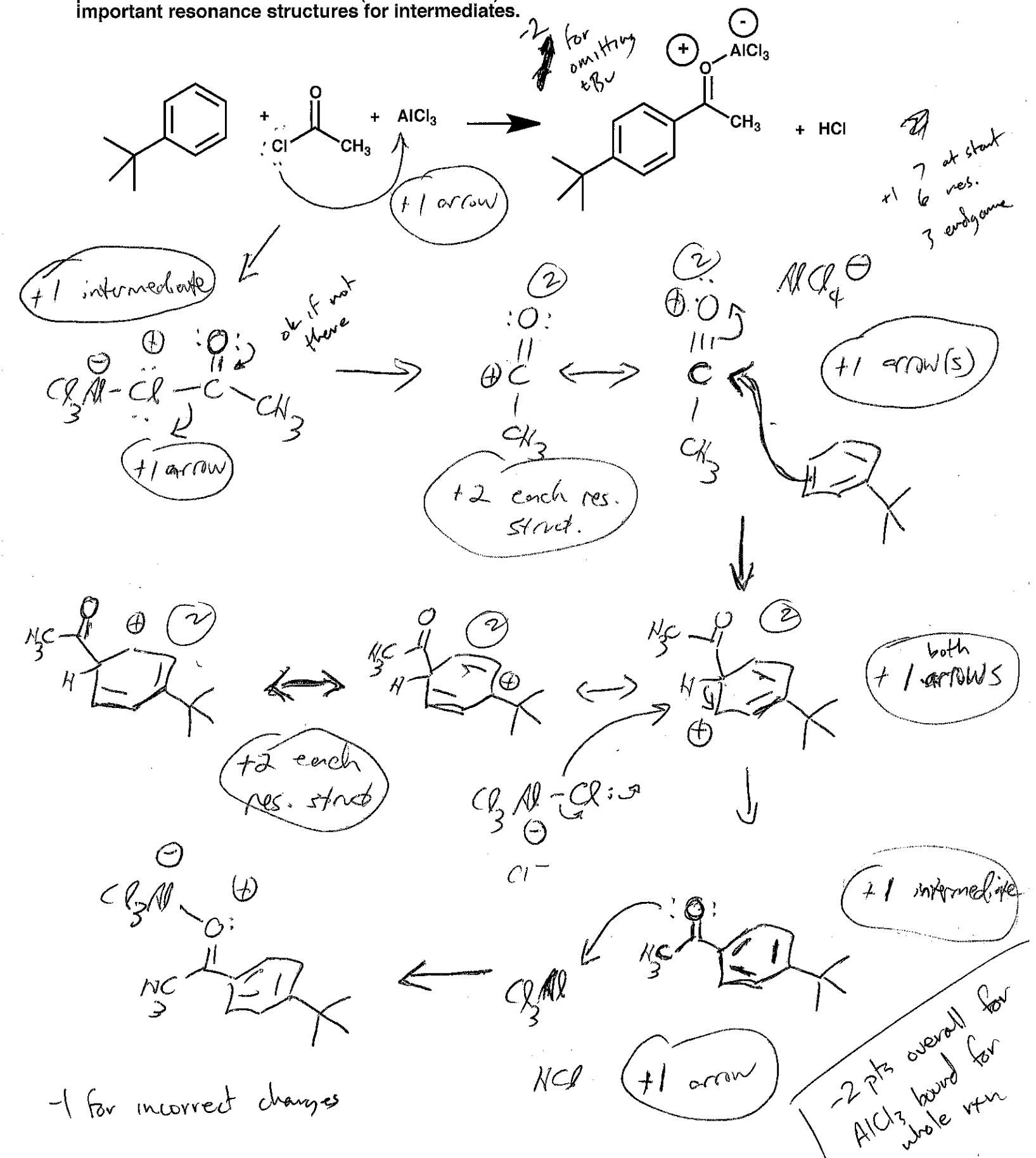
Number of proton resonances = 4 (+5)




+1 for each correct set (+4 total)

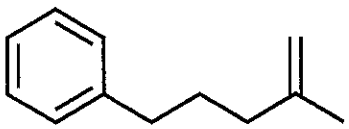
Name _____

**4. (17 points) We have learned that an acyl group can be added to an aromatic ring via a two-step procedure ("Friedel-Crafts acylation"). Shown below is an example of the first step in such a procedure; the second step involves addition of water to generate the final product. Provide a mechanism (curved arrows) for the reaction shown below. Draw all important resonance structures for intermediates.**



Name _____

5. (7 points) Propose a structure for product X formed in the reaction shown below. Your proposal should be consistent with the available data.



cat. $H_2SO_4$ → Product X ($C_{12}H_{16}$)

The $^1H$ NMR spectrum of the starting material includes the following features:

Three resonances in the range δ7-8, with a 1:2:2 integration ratio

Two resonances in the range δ5-6, each with integration for 1 H

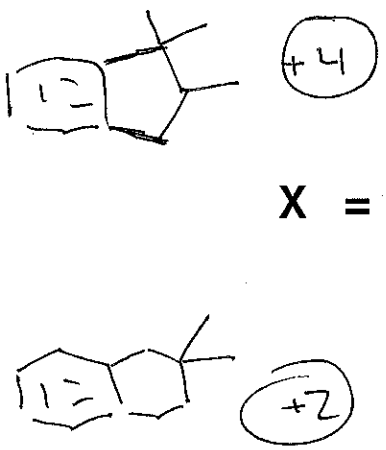
Several resonances in the range δ0-2, with integration for a total of 9 H.

The $^1H$ NMR spectrum of product X includes the following features:

Four resonances in the range δ7-8, each with integration for 1 H

No resonances in the range δ5-6

Several resonances in the range δ0-2, including a singlet with integration for 6 H and other resonances with integration for a total of 6 H.



Name _____

6. (28 points) For each of the molecules indicated, place as many of the indicated numerals as appropriate on the line below the structure

1 = Consistent with an IR signal at 3400 $cm^{-1}$

2 = Consistent with an IR signal at 3300 $cm^{-1}$

3 = Consistent with an IR signal at 3050 $cm^{-1}$

4 = $^{13}C$ NMR spectrum contains 3 resonances

5 = $^{13}C$ NMR spectrum contains 6 resonances

6 = $^{13}C$ NMR spectrum contains 7 resonances

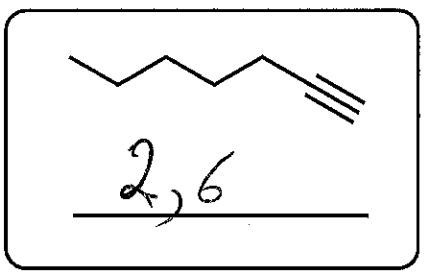
7 = One $^{1}H$ resonance disappears after the sample is shaken with a few drops of $D_2O$

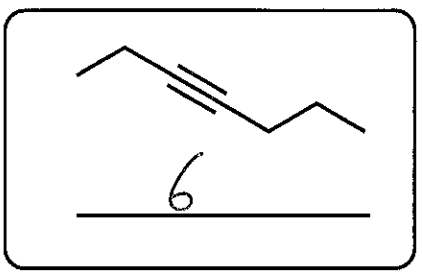
8 = One $^{1}H$ NMR resonance in the range $\delta$4.5-6.0; all other resonances $\delta < 2.5$

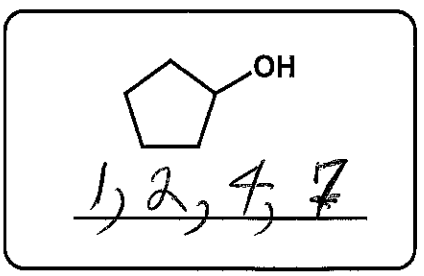
9 = $^{1}H$ NMR spectrum is two triplets, one at $\delta$3.7 and the other at $\delta$1.8

+2 for each correct

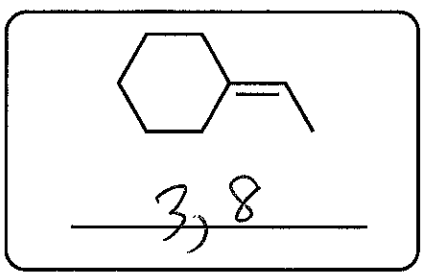
−1 pt. for incorrect

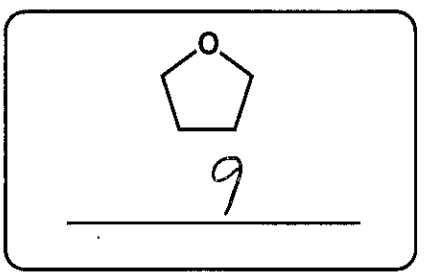

2, 6


6

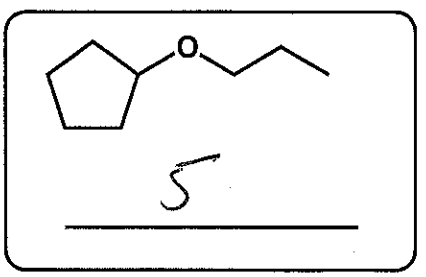


1, 2, 4, 7

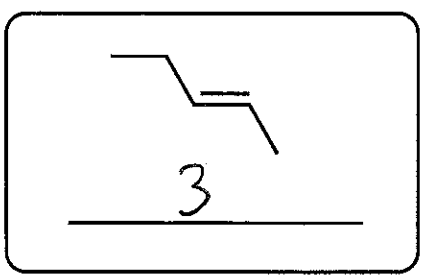

3, 8

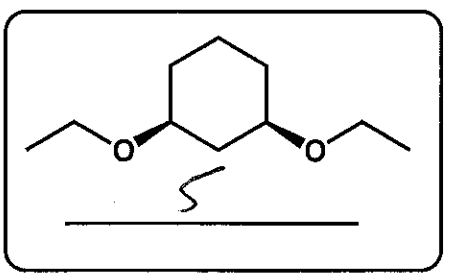


9

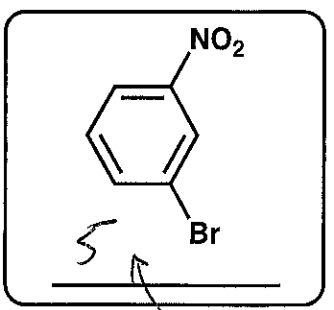


5


3



5



5

3 = +0 pts.