

NAME: _____

Email: _____

The exam must be written in ink. You have 2 hours to complete the exam.

CHEM 610B

Exam 1

Spring 2000

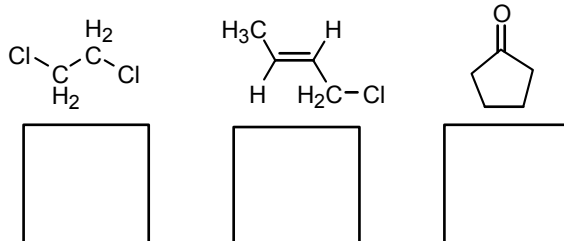
Instructor: Dr. Pagenkopf

Page	Possible Points	Score
1	20	
2	15	
3	15	
4	25	
5	20	
6	25	
7	25	
8	5	
9	15	
Total	165	

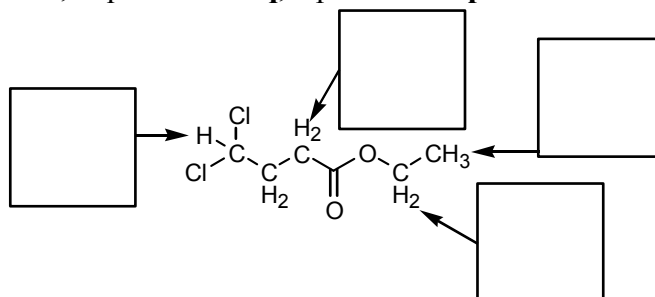
T-score

Question 1 (20 points). Miscellaneous NMR questions.

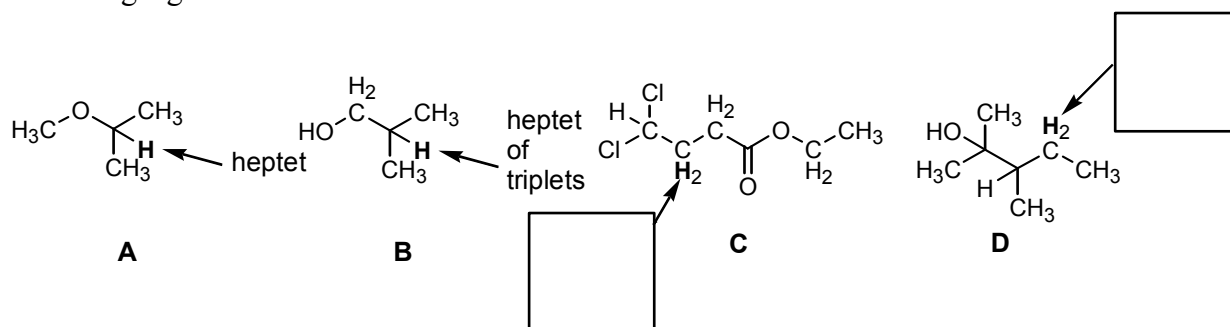
a) In the box below each molecule, indicate how many sets of equivalent hydrogens the molecule has. Each set will give rise to a different resonance signal in the ^1H NMR spectra.



b) The $n+1$ rule says that the ^1H NMR signal of a hydrogen or set of hydrogens is split into $(n + 1)$ peaks by a nonequivalent set of n equivalent neighboring hydrogens. In each box indicate what the expected splitting pattern would be for each set of indicated hydrogens. Indicate a singlet with **s**, a doublet with **d**, a triplet with **t**, a quartet with **q**, a pentet with **p**, etc.



c) Remember that splitting by adjacent hydrogens occurs according to the $n + 1$ rule only when the hydrogens are equivalent. Each different *set* of hydrogens splits a signal independently. In molecule **A** the indicated hydrogen is a heptet. In molecule **B** the indicated hydrogen is a heptet of triplets (or a triplet of heptets) but not a "nine-tet". Keeping the additive splitting in mind, indicate the splitting of the following signals in molecules **C** and **D**.



d) Would you expect the two methylene protons (the bold ones) in trifluoroethanol to resonate **upfield** (towards the right of the spectra, smaller ppm) or **downfield** (towards the left of the spectra, bigger ppm) relative to those in ethanol? Circle either downfield or upfield.



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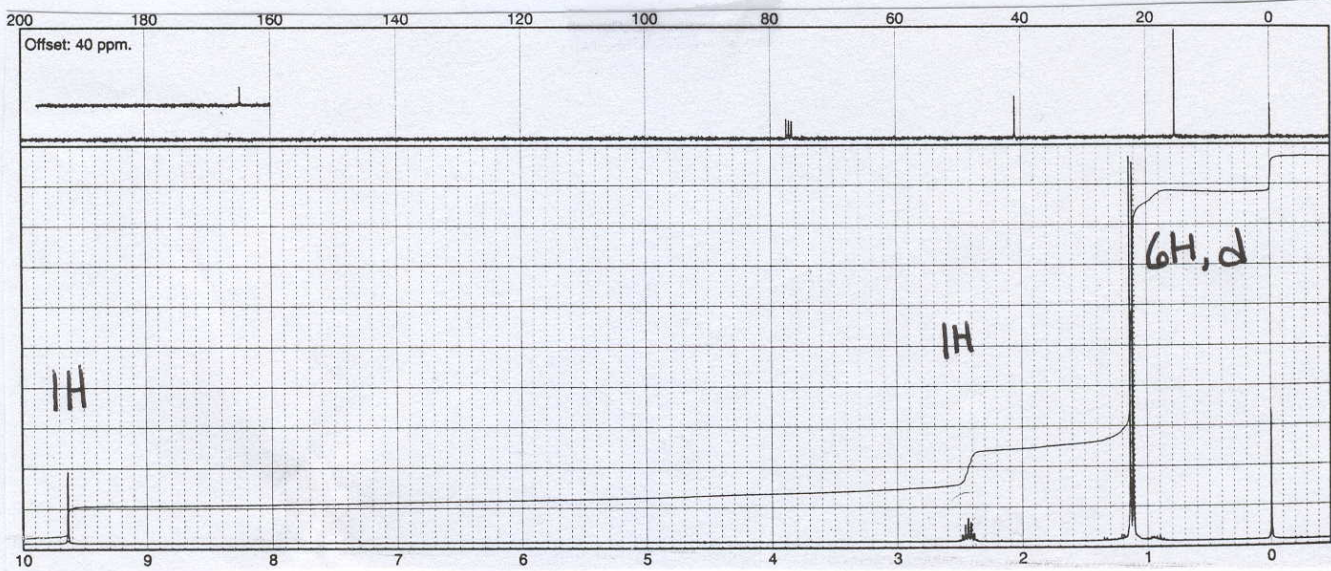
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Question 2 (15 points). Below is the NMR spectra of a molecule that reacts with Grignard reagents and may be oxidized by chromic acid. Formula C_4H_8O . Draw the structure.

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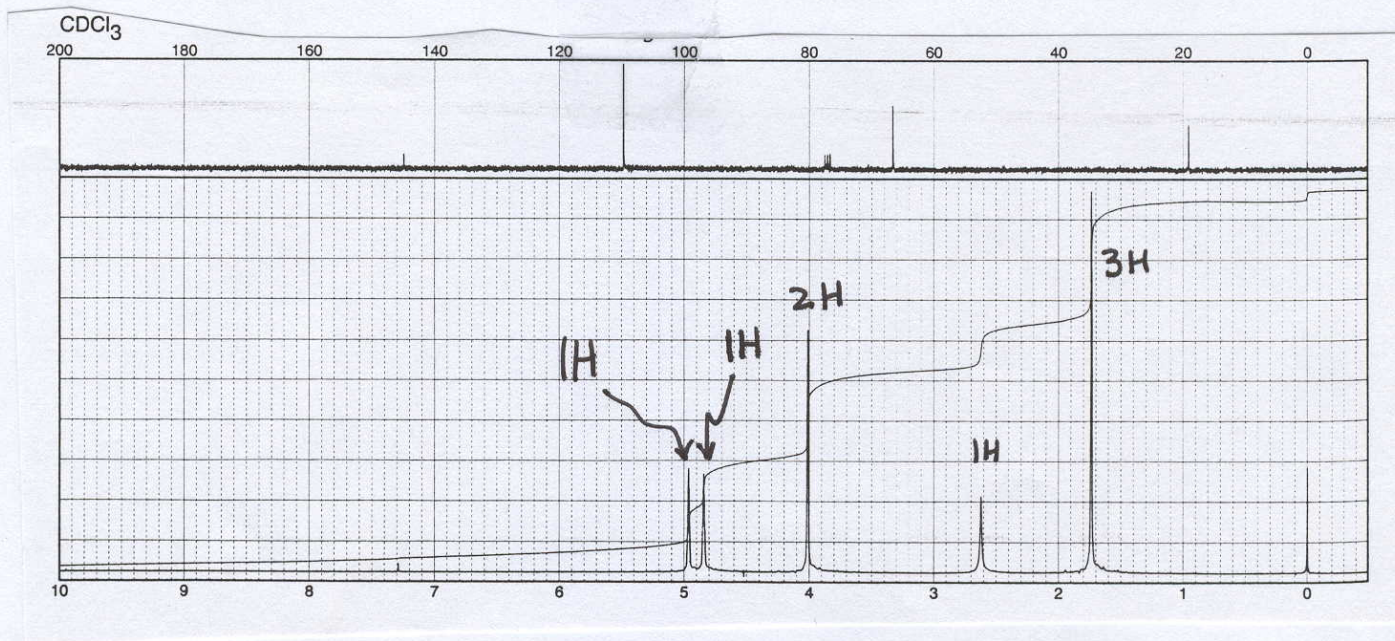
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Question 3 (15 points). Below is the NMR spectra of a molecule that reacts with one equivalent of bromine and reacts with sodium metal to release hydrogen gas. Formula C_4H_8O . Draw the structure. The signal at 2.7 readily exchanges with D_2O .

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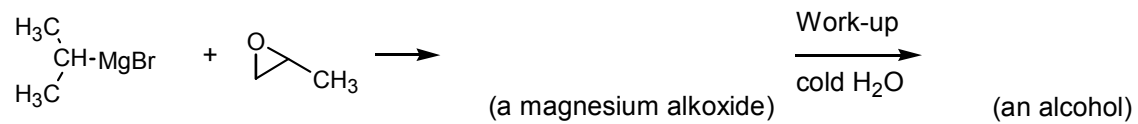
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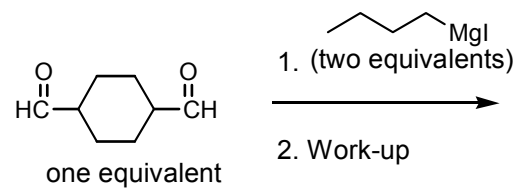


Question 4 (25 points). Grignard reactions. Draw the major product(s) expected from each of the following reactions.

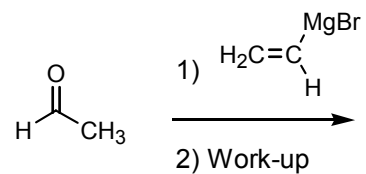
a)



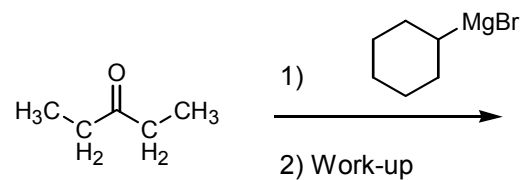
b)



c)



d)

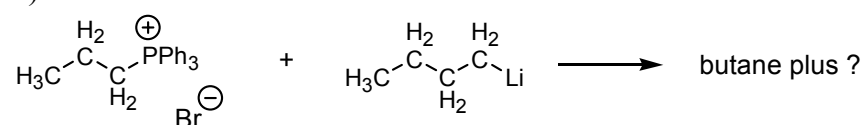


Question 5 (20 points). Wittig Reactions. Draw the major product(s) expected from each of the following reactions.

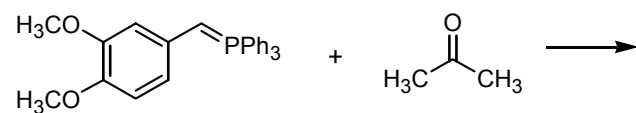
a)



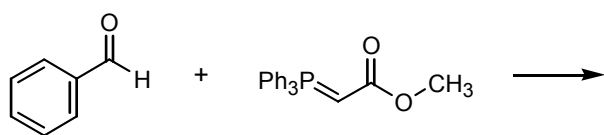
b)



c)

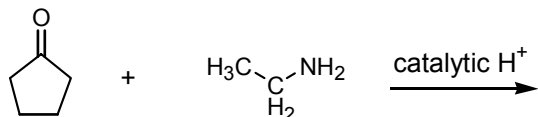


e)

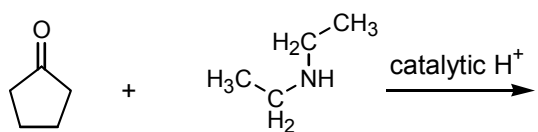


Question 6 (25 points). Miscellaneous reactions. Draw the major product(s) expected from each of the following reactions.

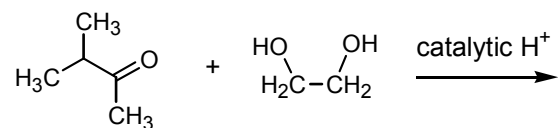
a)



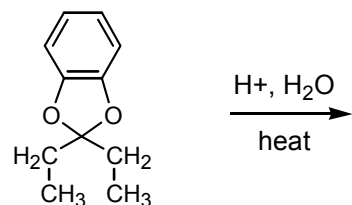
b)



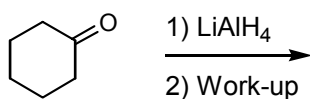
c)



d) (Show both organic molecules from the hydrolysis of the acetal).

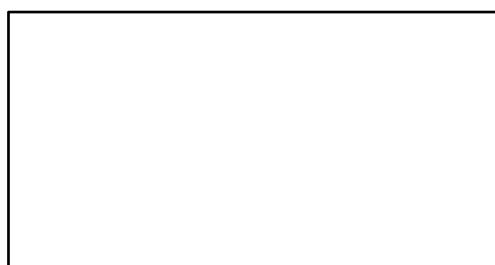
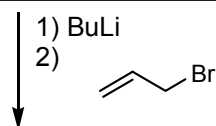
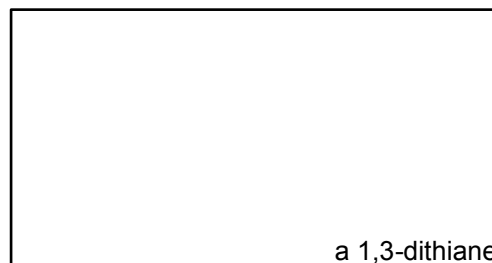
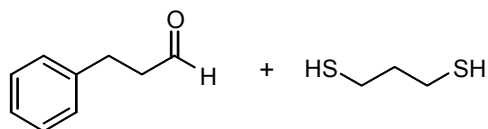


e)



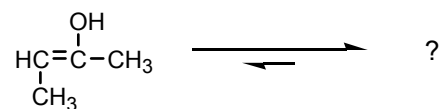
Question 7 (25 points). Miscellaneous reactions. Draw the major product(s) expected from each of the following reactions.

a)

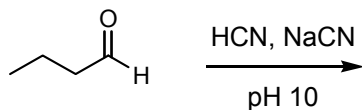


show the product that does NOT contain sulfur

b) The following enol is in equilibrium with its corresponding ketone. Draw the ketone.

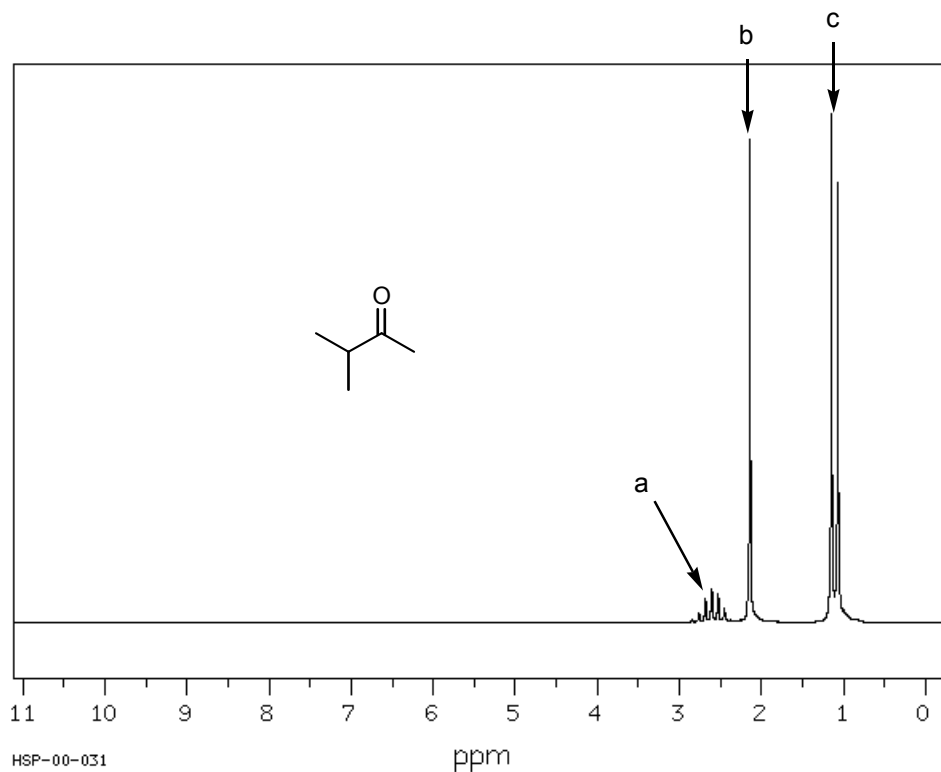


c)



Question 8 (5 points, no partial credit). 3-Methyl-2-butanone is dissolved in D_2O under basic conditions (that facilitate tautomerization between the enol and keto forms) so that the carbonyl α -hydrogens are exchanged for deuterium. Which signals in the 1H NMR spectrum of the deuterium incorporated ketone will disappear after the deuterium exchange is complete? Remember that the deuteriums will not show up in the 1H NMR.

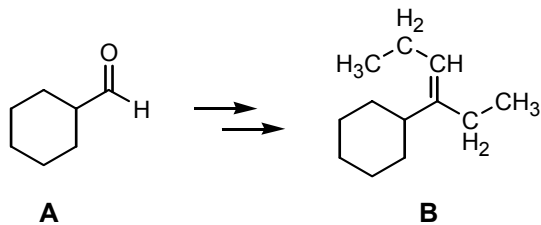
List all the signals (a, b, c) that will disappear: _____



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Question 9 (15 points). Propose a synthesis of **B** starting from **A**. You may use any reagents you want.



End of exam.