Chemistry 232-001 (Prof. Grossman's Section)

Second Examination

March 5, 2007

Name (please PRINT LEGIBLY) _____
(last) (first)

Student ID #_____

Problem	Score	
1(a–d).	_____	/20
2(a–e).	_____	/25
2.	_____	/20
3.	_____	/15
4.	_____	/15
5(a–b).	_____	/10
6(a–c).	_____	/15
Total.	_____	/120

Please observe the following.

1) Write LARGE and LEGIBLY. This will help me assign partial credit.

2) READ THE INSTRUCTIONS to each question CAREFULLY before answering. Many, many points are not awarded on each exam because of the failure of students to read the instructions.

TABLE OF ATOMIC WEIGHT MULTIPLES.

C_2	24	O_1	16
C_3	36	O_2	32
C_4	48	O_3	48
C_5	60	O_4	64
C_6	72	O_5	80
C_7	84	O_6	96
C_8	96		
C_9	108	N_1	14
C_{10}	120	N_2	28
C_{11}	132	N_3	42
C_{12}	144	N_4	56
C_{13}	156	N_5	70
$^{35}Cl_1$	35	$^{79}Br_1$	79
$^{35}Cl_2$	70	$^{79}Br_2$	158

TABLE OF IR STRETCHES IN INTERPRETABLE REGION.

Functional Group	Absorbance
X–H region	2800–3500 cm^{-1}
O–H alcohol	about 3500 cm^{-1}, strong and broad
N–H	about 3300 cm^{-1}, strong
C–H	2850–3300 cm^{-1}, strong to moderate
C≡C–H	3300 cm^{-1}
C=C–H	3000–3100 cm^{-1}
$C(sp^3)$–H	2850–3000 cm^{-1}
O=C–H	2750 cm^{-1}
O–H carboxylic acid	2800–3500 cm^{-1}, strong and *very* broad
C(sp) region	2200–2300 cm^{-1}
C≡N	about 2250 cm^{-1}, moderate
C≡C	about 2200 cm^{-1}
R–C≡C–H	moderate
R–C≡C–R	no absorption seen
$C(sp^2)$ region	1500–1800 cm^{-1}
C=O	1670–1780 cm^{-1}, *very* strong
acyclic and 6–membered cyclic ketones	1715 cm^{-1}
3– to 5–membered cyclic ketones	1740–1780 cm^{-1}
aldehydes RCHO	1730 cm^{-1}
esters RCO_2R'	1740 cm^{-1}
amides $RCO_2NR'_2$	1670 cm^{-1}
any C=O adjacent to C=C or phenyl	subtract 20–25 cm^{-1}, sometimes more
C=C	1500–1650 cm^{-1}
(very sharp absorption; can vary from strong absorption to none.)	

TABLE OF TYPICAL ^{1}H NMR RESONANCES.

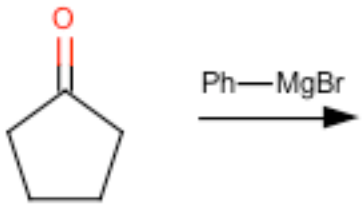
Type of C atom	Chemical Shift (δ)
saturated alkyl	0.5–1.5
C=C–C–H, O=C–C–H, C≡C–H	1.5–2.5
X–C–H (X= O, N, Hal)	2.5–4.5
C=C–H	4.5–6.5
aryl H	6.5–8.5
O=C–H	7.8–10.5
CO_2H	11–14
O–H, N–H	varies

TABLE OF TYPICAL ^{13}C NMR RESONANCES.

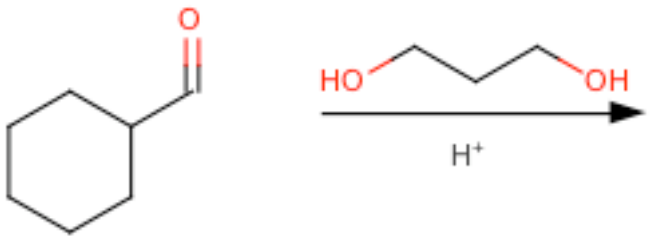
Type of C atom	Chemical Shift (δ)
alkyl C	0–50
$C(sp^3)$–N, O, Cl, Br	40–80
C≡C	60–95
C≡N	110–120
C=C	100–160
C=O	165–210

1. (5 pts. each, 20 pts. total.) Draw the ***major*** product of each of the following reactions, including the stereochemistry, if appropriate. Assume aqueous workup in each case, so your product should be neutral and should not contain any metals. **Do not draw mechanisms!**

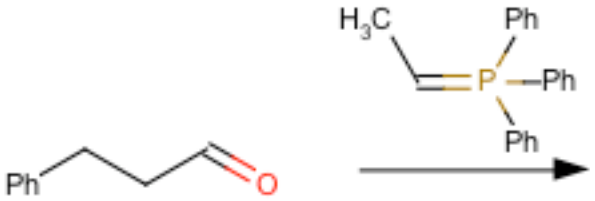
(a)



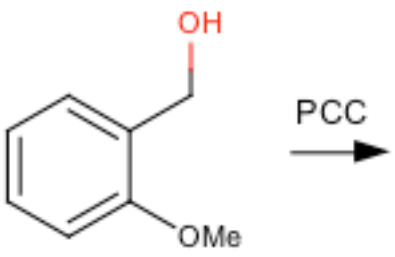
(b) Count your C atoms carefully on this one.



(c)



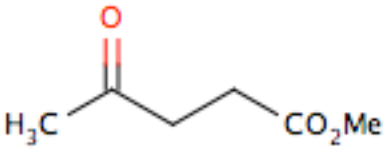
(d)

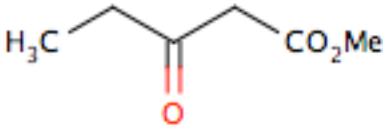


2. (5 pts. each, 25 pts. total.) Your summer job is to clean up an organic chemistry laboratory after a flood has partially destroyed the labels on many of the bottles. In each problem below, **choose a method** for distinguishing the two possibilities by MS, IR, ^{1}H NMR, or ^{13}C NMR, and precisely **describe *one* feature** of the spectrum (or the absence of a feature) that will allow you to identify the sample unambiguously.

Common Error Alert: Your response should tell me what you see in the *spectrum* of the compound. Don't write, "The ^{1}H NMR spectrum of compound 1 will show the CH_3 at δ 2.5–4.5, but the spectrum of compound 2 will not." A spectrum does not show a CH_3. It shows resonances, absorbances, or peaks. A good response would be, "The ^{1}H NMR spectrum of compound 1 will show a resonance integrating to 3 H at δ 2.5–4.5, but the spectrum of compound 2 will not."

(a) Bottle 1 contains one of the following:

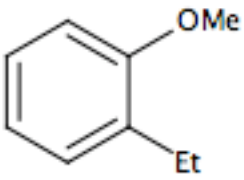


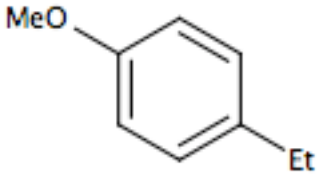


Method for distinguishing:

Difference:

(b) Bottle 2 contains one of the following:

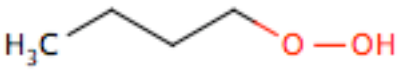




Method for distinguishing:

Difference:

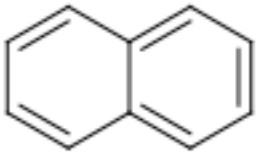
(c) Bottle 3 contains one of the following:

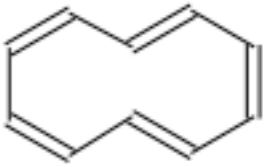


Method for distinguishing:

Difference:

(d) Bottle 4 contains one of the following:

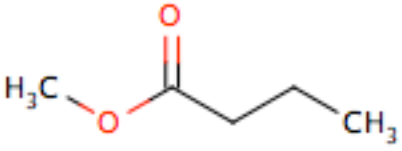


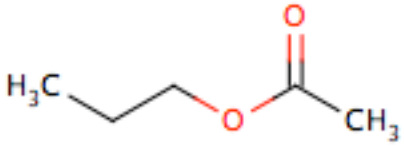


Method for distinguishing:

Difference:

(e) Bottle 5 contains one of the following:

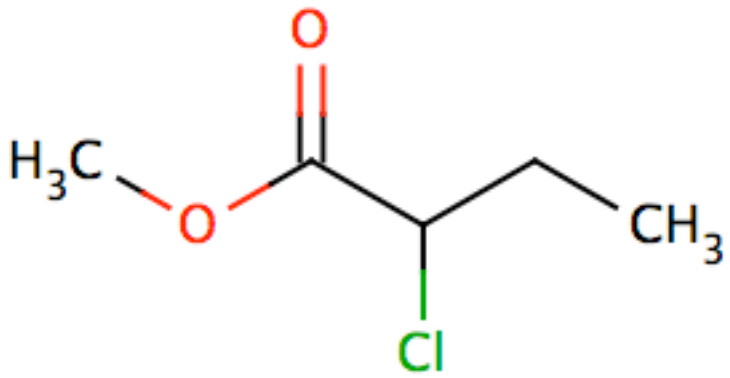




Method for distinguishing:

Difference:

2. (20 pts. total) Draw in all of the H atoms in the following compound.

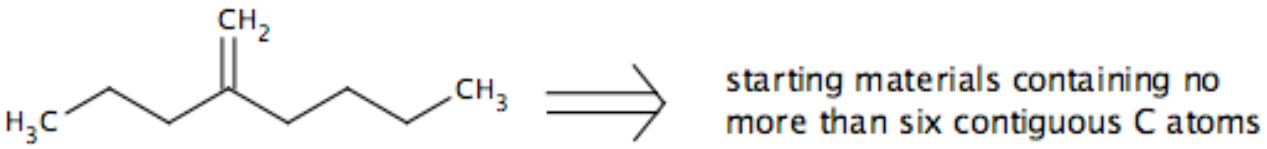


(a) (5 pts.) Label equivalent H atoms with the same letter and inequivalent H atoms with different letters, as we did in class.

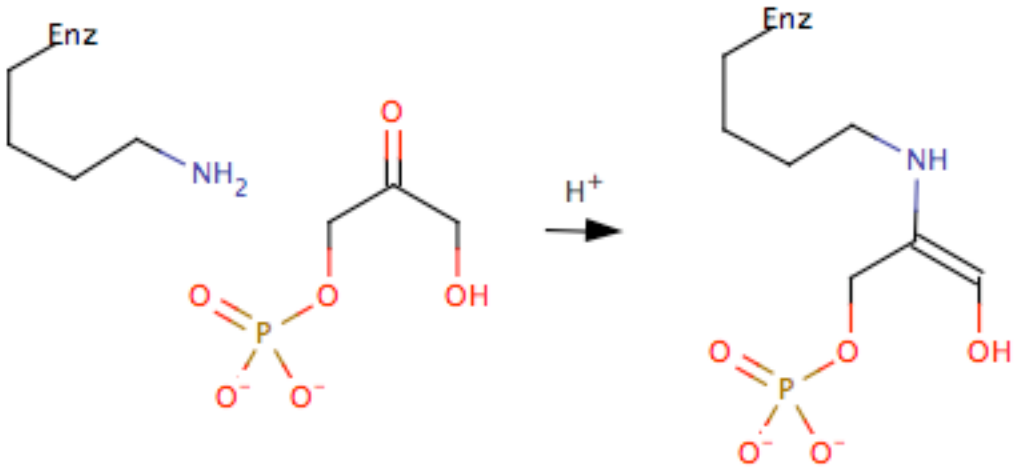
(b) (15 pts.) Predict the ^{1}H NMR spectrum of the compound, indicating the *approximate* chemical shift, integration, and multiplicity for each resonance that you expect to see. You can find a table of ^{1}H NMR chemical shifts at the front of this exam.

Type of H	δ (in ppm)	Integration	Multiplicity

3. (15 pts. total.) Design a synthesis of the following compound from the given starting materials. The synthesis will require more than one step. Show each intermediate compound and all reagents you will need for each step. (Don't panic if you can't remember the reagents for a particular step; partial credit will be given.) There may be more than one correct answer. **Do not show mechanisms. You are strongly advised to do a retrosynthetic analysis before drawing the synthetic sequence in the forward direction.**



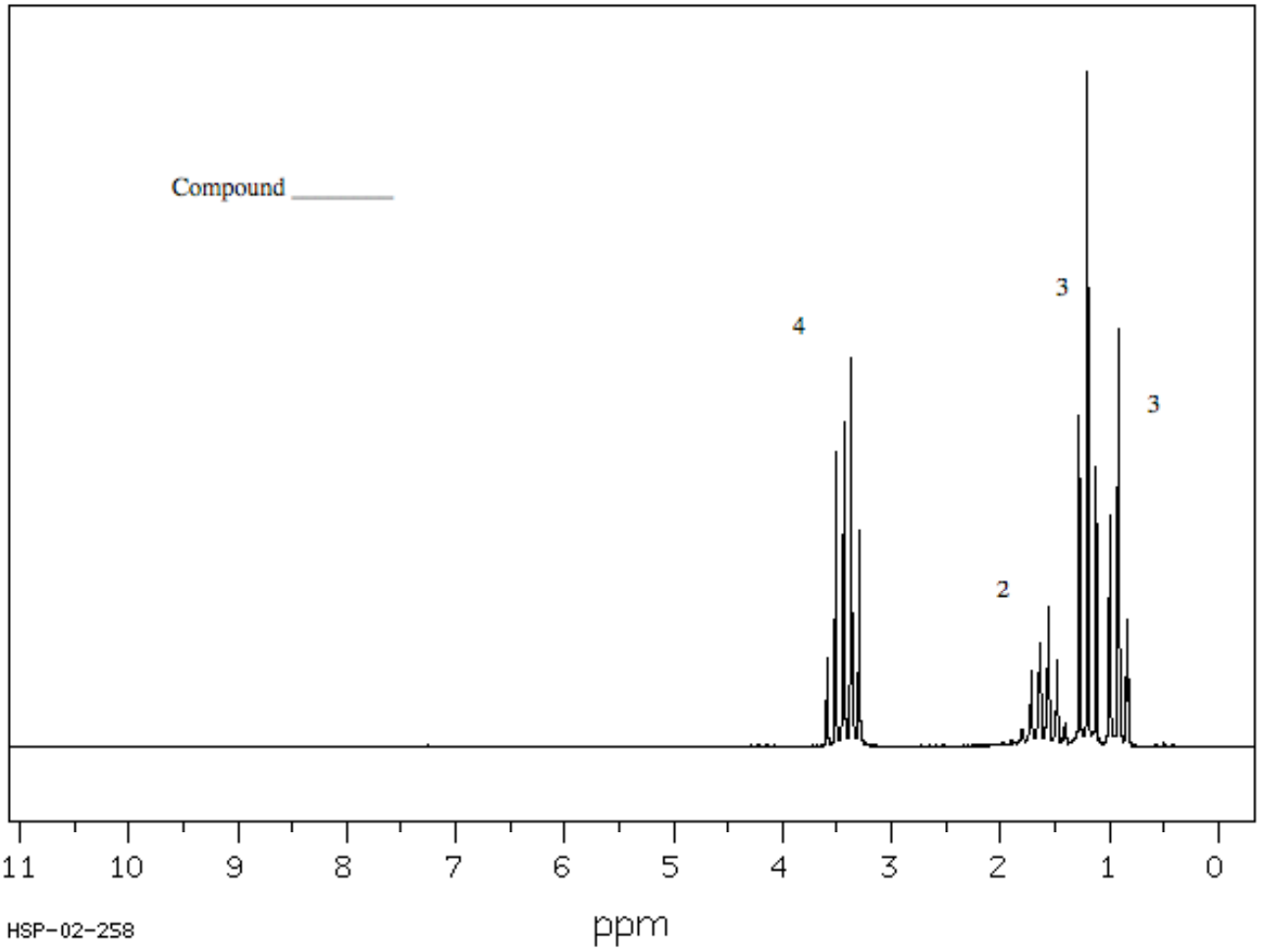
4. (15 pts.) An enzyme called aldolase converts two three-carbon sugars, dihydroxyacetone phosphate (DHP, shown below) and glyceraldehyde-3-phosphate (not shown), into the six-carbon sugar fructose-1,6-diphosphate (not shown). The first step in this C–C bond-forming reaction is to convert DHP into an enamine. The enzyme uses the $(CH_2)_4NH_2$ side chain of a lysine residue and an H^+ in the enzyme's bonding pocket to convert the ketone into an enamine.

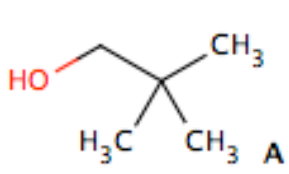


Draw a reasonable mechanism for this reaction. Use the conventional curved arrows to show the movement of electrons in each step. **You are strongly advised to obey Grossman's rule.**

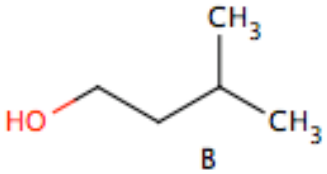
5. (5 pts. each, 10 pts. total) Indicate which of the compounds below each ^{1}H NMR spectrum gives rise to the spectrum. The integrations are given by the numbers next to each resonance.

(a)

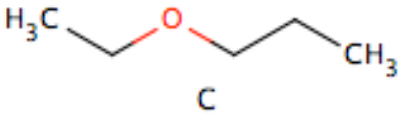




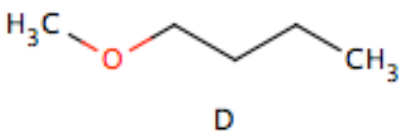
A



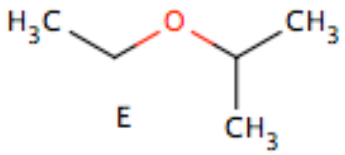
B



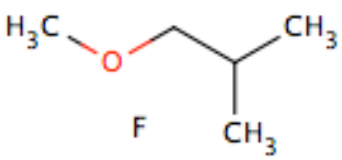
C



D

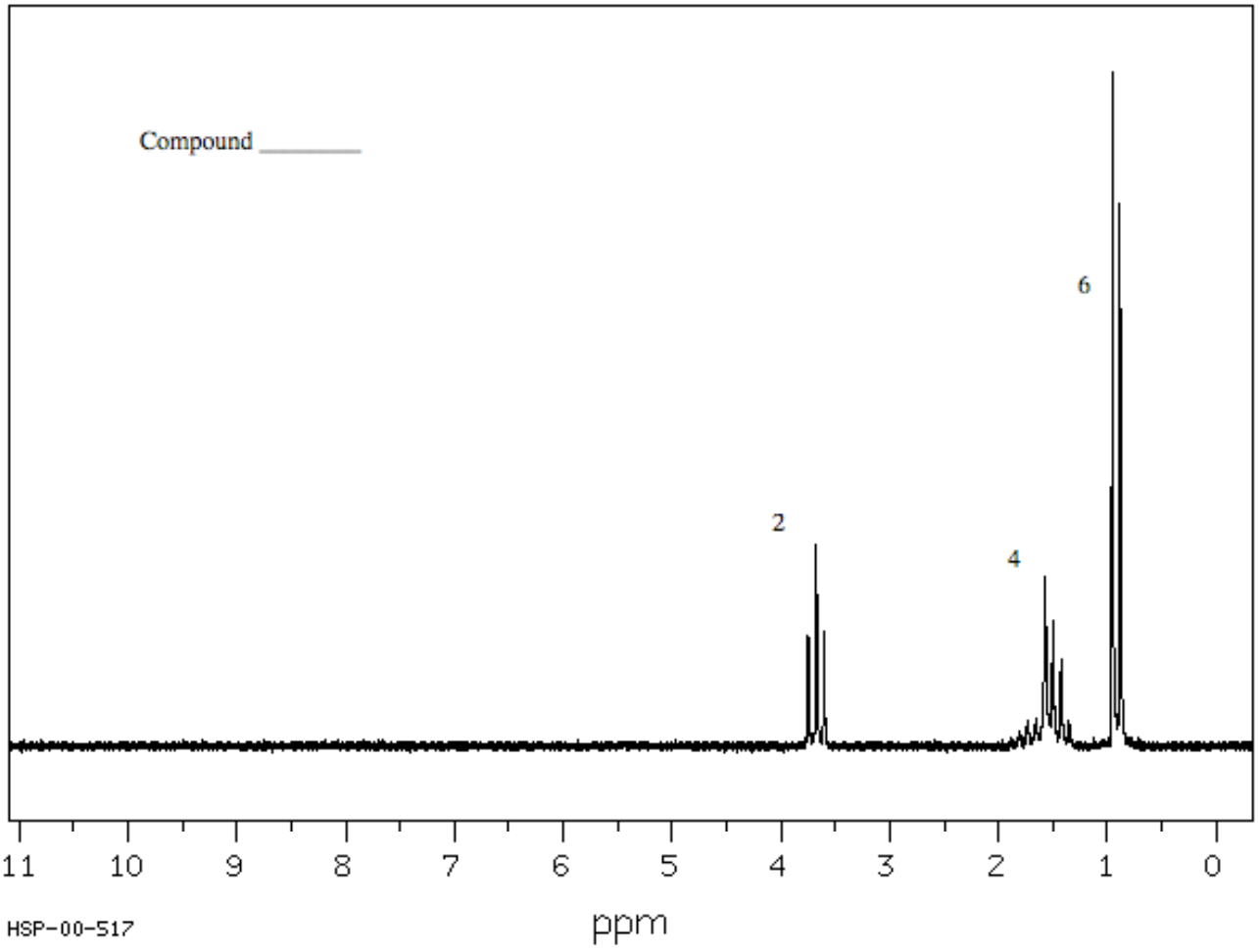


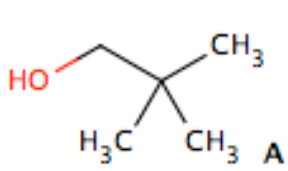
E

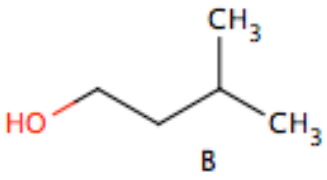


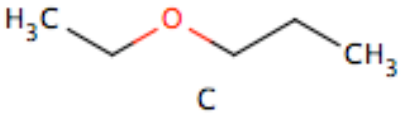
F

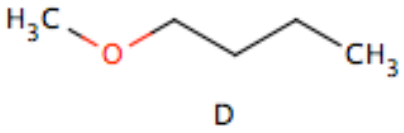
(b)

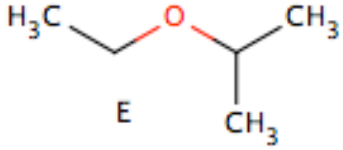


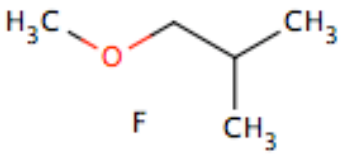








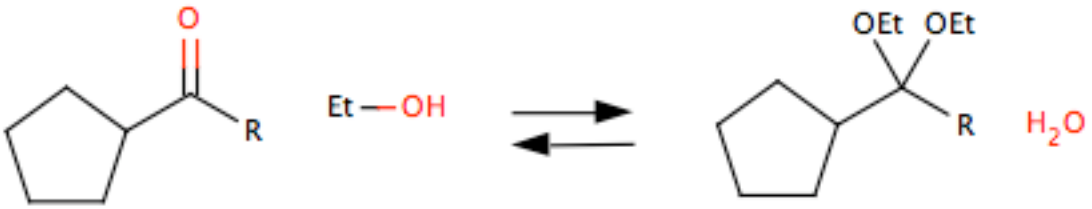




(This is the same set of compounds as in (a).)

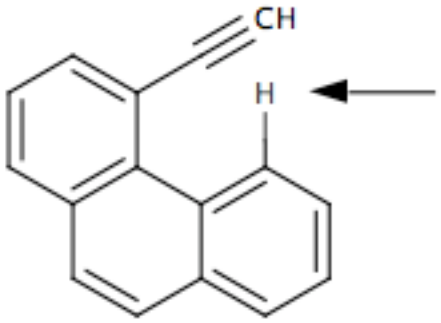
6. (5 pts. each, 15 pts. total) Explain each of the following observations in one or two coherent, grammatically correct English sentences free of misspellings. Feel free to draw pictures to illustrate your explanations.

(a) The equilibrium constant of the reaction below is *smaller* when R = CH_3 than when R = H.



(b) The reaction shown in part(a) works well in either direction under acidic conditions, but not under basic conditions.

(c) In the compound below, the indicated H atom appears considerably further *downfield* than the corresponding H atom in the compound that does not have the C≡C triple bond.



END OF EXAM