CHEM 2410 – Organic Chemistry 1 – Fall 2016

Instructors: Erin Whitteck & Paul Bracher

Hour Examination #4

Wednesday, November 30th, 2016

6:10–8:10 p.m. in the Lecture Halls at Saint Louis University

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use one letter-sized sheet of hand-written notes (on the "official" template) and your plastic model kit. The only electronic resource permitted is a TI-30XA, TI-30XIIS, or TI-30XS calculator.
- You may not communicate with others.
- Your exam answer sheet may be copied or scanned. The examination room may be photographed or videotaped.

Problem	Points Earned	Points Available
I		66
II		4
III		9
IV		9
V		12
TOTAL		100

Questions, Required Information, Supplementary Explanation, Grading Notes, Where You've Seen It

Problem I. Multiple Choice (66 points total). Correct answers score +3 points, answers of 'E' score +1 point, and incorrect answers score 0 points. For each question, select the best and most complete answer of the choices given. Bubble the answer, darkly, in the space provided on the answer sheet.

(1) ___A___ Which of the following statements is correct?

(A) a compound with a chemical shift of 7.20 ppm collected on a 300 MHz NMR spectrometer will also have a chemical shift of 7.20 ppm on a 700 MHz spectrometer

(B) carbon atoms with six protons and six neutrons are NMR active

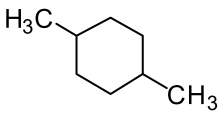
(C) peaks observed in IR spectroscopy represent electronic transitions between molecular orbitals

(D) the alignment of nuclear spin against an external magnetic field is lower-in-energy than alignment with the external magnetic field

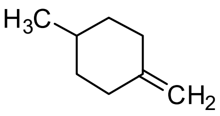
A signal with a chemical shift of 7.20 ppm will be the same no matter what instrument is used, as the calculation to ppm takes into account the field strength of the instrument. ^{12}C atoms are not NMR active. Peaks observed in IR spectroscopy represent transitions between vibrational states. Alignment of nuclear spin with the external field is more energetically favorable than against the external magnetic field.

Where you've seen it: Fall 2014 Exam $^{\#}$4, Problem I-4.

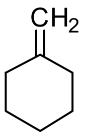
(2) ___B___ Which of the following compounds would give rise to a ^{13}C NMR spectrum with six signals?



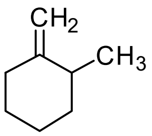
(A)



(B)



(C)

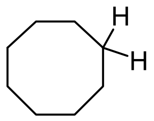


(D)

Compound (A) would give rise to 3 peaks. Compound (B) would give rise to 6 peaks. Compound (C) would give rise to 5 peaks. Compound (D) would give rise to 8 peaks.

Where you've seen it: Summer 2016 Exam $^{\#}$4, Problem I-6

(3) A Two of the sixteen hydrogen atoms in compound **A**, cyclooctane, are drawn explicitly below. What is the multiplicity of the signal corresponding to the drawn hydrogen atoms?



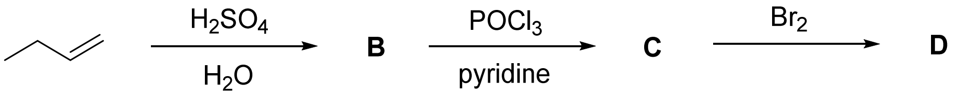
A

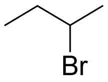
(A) singlet
(B) doublet
(C) triplet
(D) triplet of triplets

All of the hydrogens in cyclooctane are equivalent, so there is no spin-spin splitting in the ^{1}H NMR spectrum and all of the hydrogens give rise to a single singlet peak.

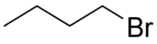
Where you've seen it: Fall 2014 Exam $^{\#}$4, Problem I-2.

(4) C What is compound **D**, the major product of the following sequence of reactions?

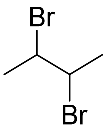




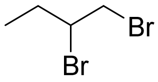
(A)



(B)

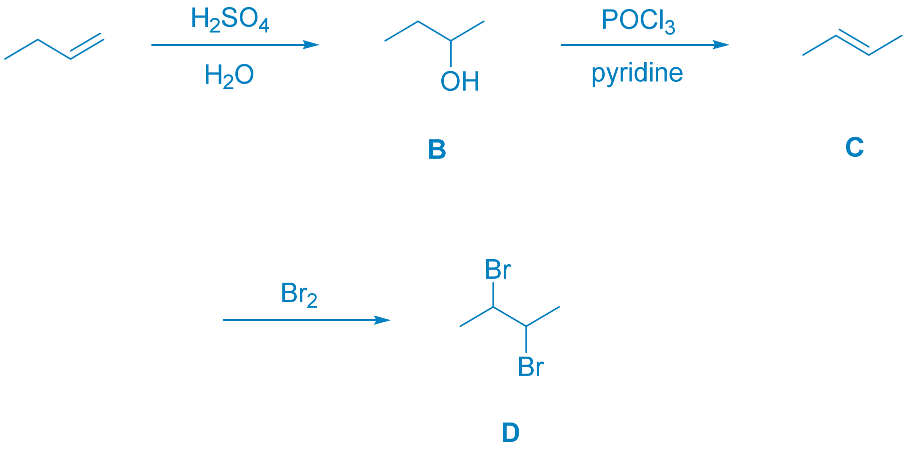


(C)



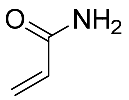
(D)

The reaction sequence is as follows:

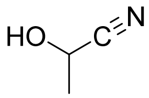


Where you've seen it: Format identical to Fall 2016 Exam #3, Problem I-20. All of these reactions were covered separately in various lecture slides and problems throughout the semester.

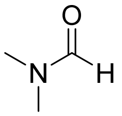
(5) C Which of the following compounds is most easily distinguished from the other molecules using mass spectrometry as the sole analytical technique?



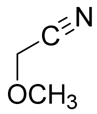
(A)



(B)



(C)



(D)

Molecules (A), (B), and (D) have a molecular formula of C_3H_5NO and a molecular weight of 71 a.m.u. Molecule (C) has a molecular formula of C_3H_7NO and a molecular weight of 73 a.m.u. Mass spectrometry distinguishes between molecules based on molecular weight, therefore only molecule (C) could easily be distinguished from the other molecules.

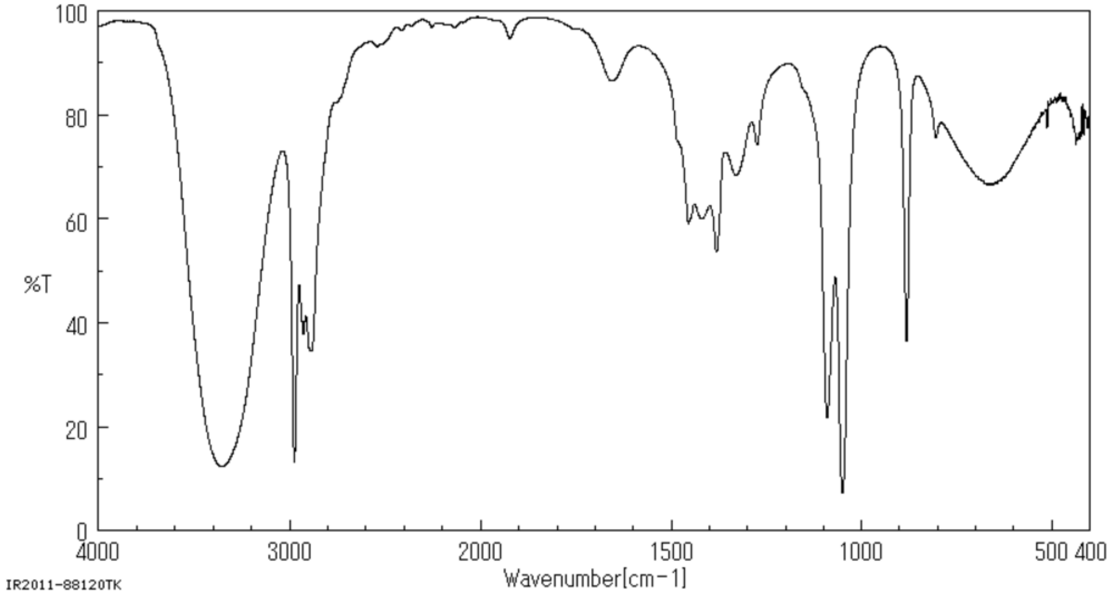
Where you've seen it: Similar to Fall 2016 Lecture 33 clicker question.

(6) A

What changes would be expected in the IR spectrum of the reaction mixture if ethanol were treated with pyridinium chlorochromate (PCC)?

$$CH_3CH_2OH \xrightarrow{\text{PCC}} \mathbf{E}$$

IR Spectrum of ethanol:



Source: Spectral Database for Organic Compounds, Ethyl Alcohol, #1300
http://sdbs.db.aist.go.jp/

Source: Spectral Database for Organic Compounds, Acetaldehyde, #305
http://sdbs.db.aist.go.jp/

(A) the disappearance of the broad peak at 3358 cm^{-1} and the appearance of an intense peak at 1727 cm^{-1}
(B) the disappearance of the broad peak at 3358 cm^{-1} and the appearance of a very broad peak from 2500–3500 cm^{-1}
(C) the disappearance of the peak at 2974 cm^{-1} and the appearance of an intense peak at 1715 cm^{-1}
(D) the disappearance of the peak at 2974 cm^{-1} and the appearance of a sharp peak at 2254 cm^{-1}

This reaction involves the oxidation of a primary alcohol to an aldehyde. As a result the alcohol peak at 3358 cm^{-1} would disappear and a carbonyl peak around 1727 cm^{-1} would appear.

Where you've seen it: Similar to the monitoring of a reaction described in Fall 2016 Lecture 34 Slide 40.

(7) C

MCHM is a chemical used to wash coal of materials whose presence would contribute to increased pollution during combustion. In 2014, a large quantity of MCHM leaked from a holding tank into the ground by the Elk River in West Virginia, rendering the tap water in the city of Charleston undrinkable. MCHM has 1 degree of unsaturation (Ω = RAPB = 1) and a molecular ion at m/z 128. Which of the following is the molecular formula of MCHM?

Source: Wikipedia
https://en.wikipedia.org/wiki/2014_Elk_River_chemical_spill

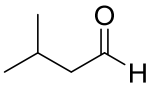
(A) $C_6H_8O_3$
(B) $C_7H_{12}O_2$
(C) $C_8H_{16}O$
(D) $C_6H_{15}N_3$

Compound (A) is 128 a.m.u. and RAPB = 3. Compound (B) is 128 a.m.u. and RAPB = 2. Compound (C) is 128 a.m.u. and RAPB = 1. Compound (A) is 129 a.m.u. and RAPB = 1. MCHM is 4-methylcyclohexanemethanol.

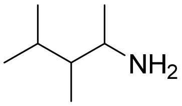
Where you've seen it: This is a matter of calculating masses and RAPB values, which we have done in many problems for Chapter 13.

(8) B

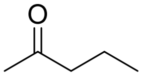
Which of the following compounds will have a signal in its ^{1}H NMR spectrum in DMSO-d_6 disappear upon the addition of deuterated water (D_2O) to the sample?



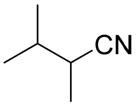
(A)



(B)



(C)



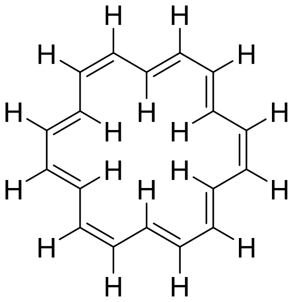
(D)

Protic hydrogens (those capable of hydrogen bonding) will exchange with deuterium when protic deuterated compounds are added to the sample. Deuterium atoms (^{2}H) do not show up in ^{1}H NMR spectra.

Where you've seen it: Summer 2016 Exam $^{\#}$4 Problem I-2. Fall 2014 Exam $^{\#}$4 Problem I-6.

(9) C

Compound **F** is 18-annulene, an aromatic compound with 18 π electrons, has a similar response to benzene in the presence of an applied magnetic field. The ^1H NMR spectrum of **F** has two signals: δ 8.9 ppm and δ −1.8 ppm. Which of the following statements is not true of compound **F**?



F

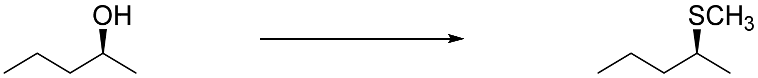
(A) the protons inside the ring are shielded compared to the protons outside of the ring
(B) there are two unique sets of protons in the molecule
(C) the induced magnetic field opposes the external field in the vicinity of protons outside the ring
(D) the IR spectrum will have stretches around 3100 cm^{-1}

There are two unique sets of protons: the protons inside the ring and outside the ring. The protons inside the ring are shielded because the induced magnetic field opposes the external magnetic field in the center of the molecule. The protons on the outside of the ring are deshielded because the induced magnetic field lines align with the applied field at around the outside edges of the molecule. The IR spectrum will contain *sp*^{2} C–H stretching around 3100 cm^{-1}.

Where you've seen it: very similar to Smith textbook Chapter 14, Problem 74. Also covered in Lecture 38 Problem Session Question 2.

(10) A

Which of the following sequences of reactions is the best choice to convert **G** to **H**?



G **H**

(A) $\xrightarrow{PBr_3}\xrightarrow[DMSO]{NaSCH_3}$

(B) $\xrightarrow[pyridine]{TsCl}\xrightarrow[DMSO]{NaSCH_3}$

(C) $\xrightarrow[H_2O]{H_2SO_4}\xrightarrow[H_2SO_4]{CH_3SH}$

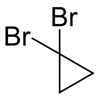
(D) $\xrightarrow{SOCl_2}\xrightarrow[H_2SO_4]{CH_3SH}$

The OH group must be replaced with a SCH_3 group with retention of stereochemistry. Typically, this will involve double inversion by two S_N2-like reactions. Here, the OH group is converted to a Br group (with inversion) by PBr_3. Then, in the second step, S_N2 displacement by thiomethoxide yields the desired product. Option (B) gives the wrong stereochemistry in the product. Options (C) and (D) are flawed for multiple reasons.

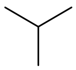
Where you've seen it: Reactions discussed in lecture and various problems.

(11) B

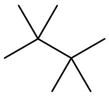
Which of the following compounds will have the <u>most</u> signals in its ^{1}H NMR spectrum?



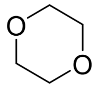
(A)



(B)



(C)

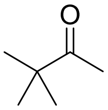


(D)

Only choice (B) possesses protons in two different electronic environments (the methyl groups are equivalent, but different from the tertiary hydrogen on the central carbon).

Where you've seen it: Fall 2015 Exam #4, Problem I-4.

(12) ____B____ Which set of m/z values below represents significant peaks in the electron-impact mass spectrum of compound **J**?

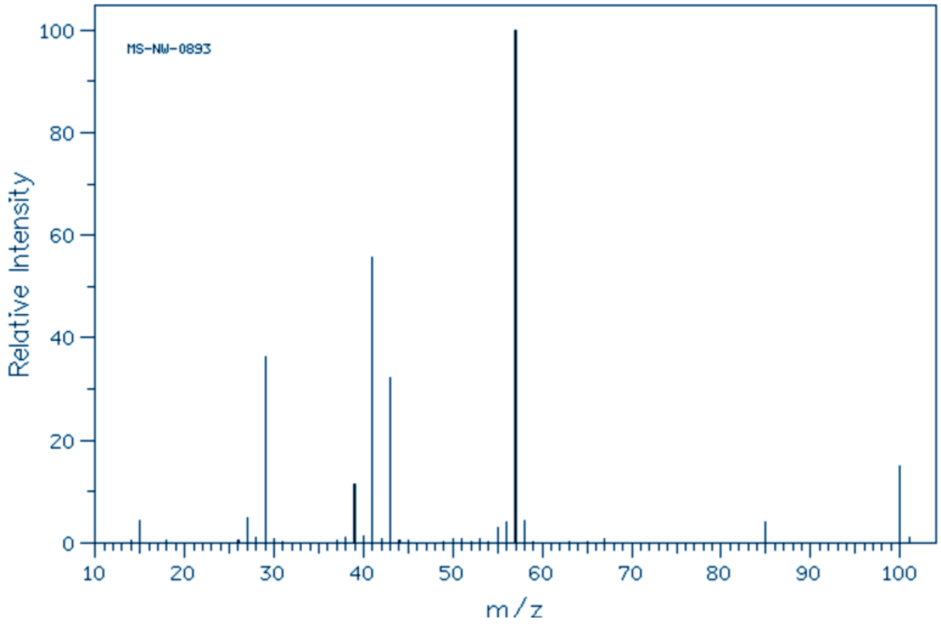


J

(A) 57, 43, 20
(B) 85, 57, 43
(C) 100, 85, 20
(D) 102, 100, 85

Carbonyl compounds tend to fragment to produce resonance -tabilized acylium ion. Ketone **J** can fragment on either side of the carbonyl carbon producing two different acylium ions. A peak at m/z 102 would exceed the mass of **J**, and there is no fragment that would correspond to m/z 20.

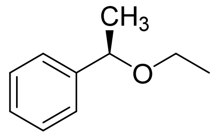
Actual EI-MS of compound **J**:



Source: Spectral Database for Organic Compounds, 3,3-dimethyl-2-butanone, #1790
http://sdbs.db.aist.go.jp/

Where you've seen it: Fall 2016 Lecture 34 clicker question 1; CYOA November 14/15.

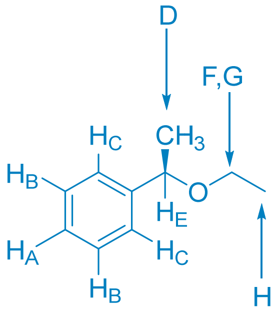
(13) C How many signals (arising from sets of inequivalent protons) appear in the ^1H NMR spectrum of compound **K**. Hint: Be careful!



K

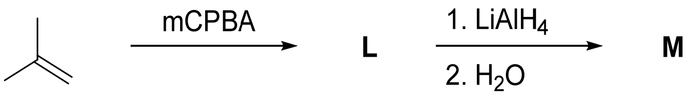
(A) 6 signals
(B) 7 signals
(C) 8 signals
(D) 9 signals

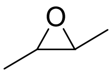
There are three sets of unique protons on the aromatic ring. The methyl group on the carbon alpha to the ring, and the proton attached to that carbon are unique. The methylene protons are diastereotopic, and the methyl protons are unique:



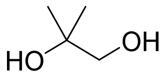
Where you've seen it: Fall 2016 CYOA session for Nov 21/22.

(14) D What is compound **M**, the major product of the following sequence of reactions?

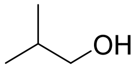




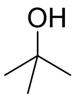
(A)



(B)

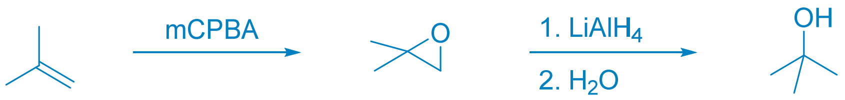


(C)



(D)

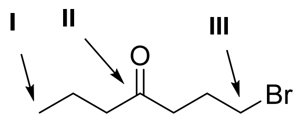
The reaction sequence is as follows:



L **M**

Where you've seen it: Format identical to Fall 2016 Exam #3 Problem I-20. All of these reactions were covered separately in various lecture slides and problems throughout the semester. Also, very similar to Fall 2016 Exam #3 roadmap problem.

(15) B Rank the labeled carbon atoms in order of increasing chemical shift (from lowest to highest value) in the ^{13}C NMR spectrum of compound **N**.



N

(A) **I < II < III**
(B) **I < III < II**
(C) **II < III < I**
(D) **II < I < III**

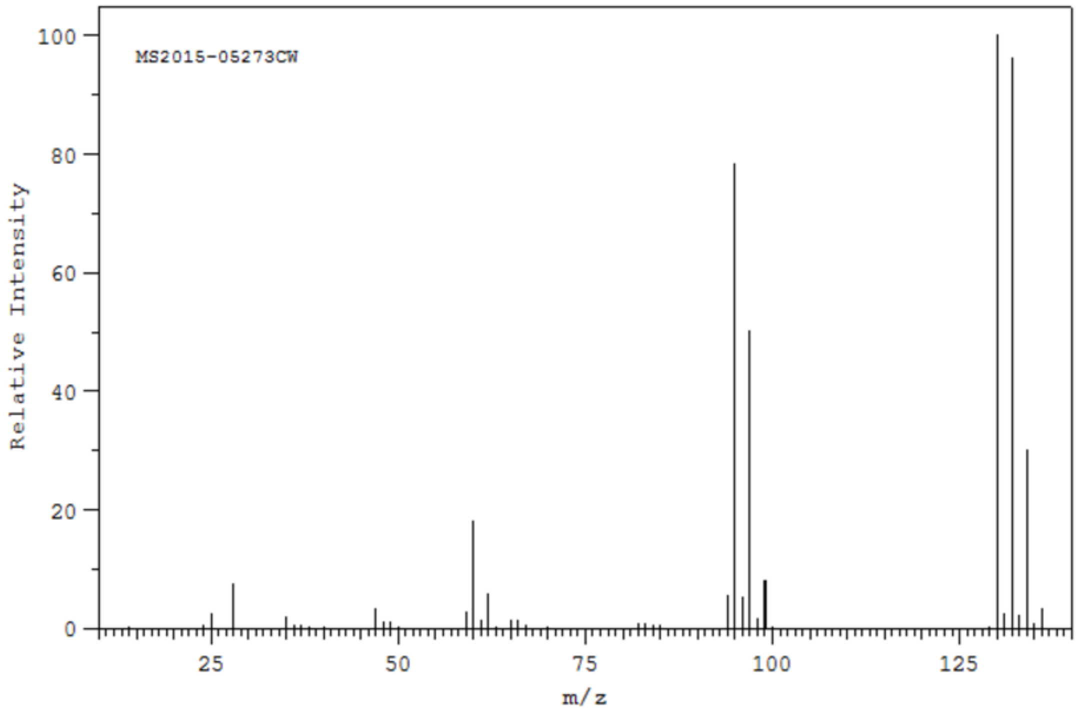
Carbon (C) will be the most shielded since it is an *sp*^{3}-hybridized carbon and is not attached to an electron-withdrawing group. Choice (B) will be more deshielded because it is attached to an electron-withdrawing bromine atom. Carbon (A) will be the most deshielded because it is a carbonyl carbon.

Where you've seen it: Fall 2016 Connect Homework Chapter 14 Problem 18.

(16) C

Compound **P** is a sweet-smelling organic liquid that was once used as an anesthetic for medical procedures and to extract caffeine from coffee beans. These uses have largely been phased out due to the identification of **P** as a health hazard and carcinogen (a compound that causes cancer) by the European Union and U.S. Environmental Protection Agency. Compound **P** is composed solely of carbon, hydrogen, and chlorine atoms. Given its mass spectrum below, which includes the molecular ion of **P**, identify how many chlorine atoms are present in the compound.

EI Mass Spectrum of Compound **P**:



Source: Spectral Database for Organic Compounds, trichloroethylene, #2151
http://sdbs.db.aist.go.jp/

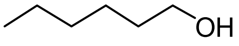
m/z	Relative Intensity
130	100.0
131	2.4
132	96.3
133	2.1
134	30.2
136	3.2

(A) one chlorine atom
(B) two chlorine atoms
(C) three chlorine atoms
(D) four chlorine atoms

The presence of M, M+2, M+4, and M+6 peaks is indicative of a compound containing three chlorine atoms. The relative ratio of the M and M+6 peaks should be ≈ $0.75^3/0.25^3 = 3^3 = 27 \approx 100.0/3.2$, matching the data provided.

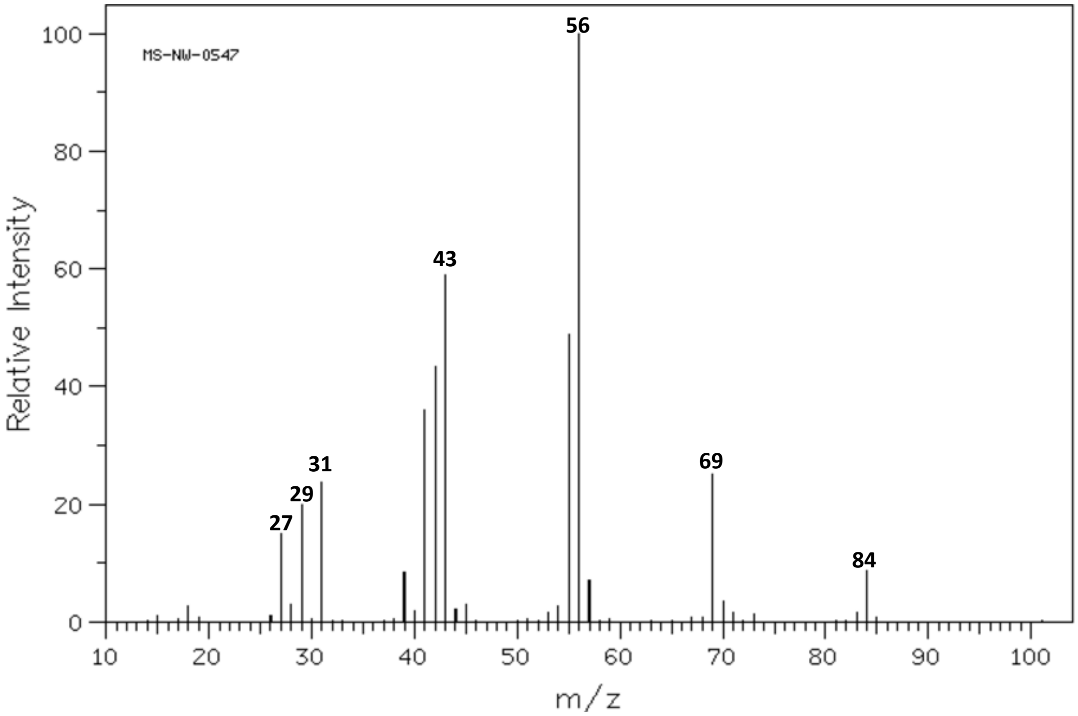
Where you've seen it: Fall 2016 Lecture 33 clicker question, CYOA November 14/15.

(17) A Which of the following species does <u>not</u> correspond to a peak in the electron-impact mass spectrum of 1-hexanol (**Q**)?



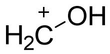
Q

EI Mass Spectrum of Compound **Q**:

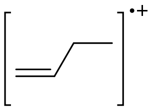


Source: Spectral Database for Organic Compounds, hexyl alcohol, #1303
http://sdbs.db.aist.go.jp/

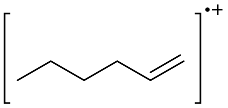
(A)



(B)



(C)

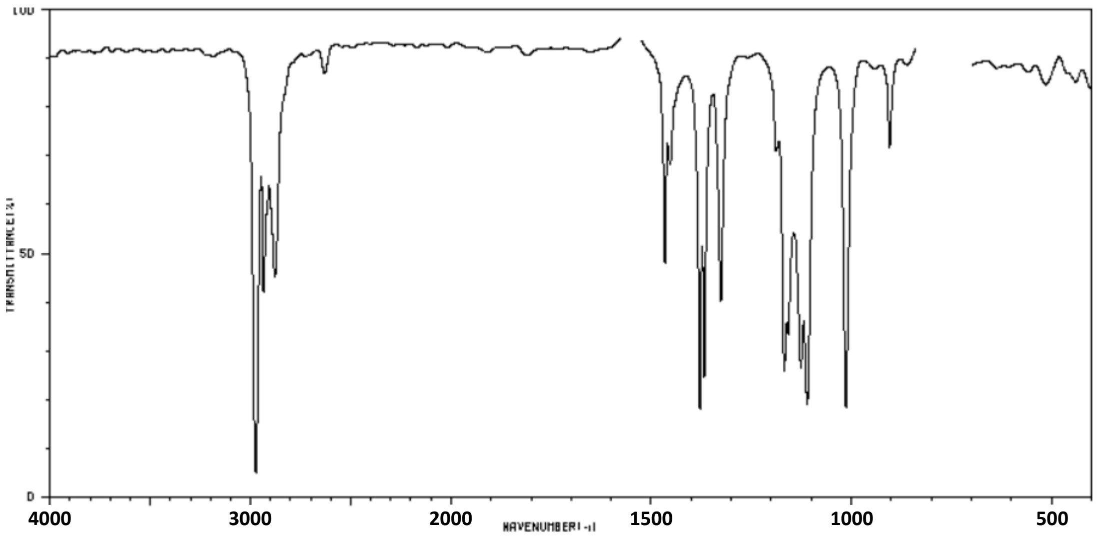


(D)

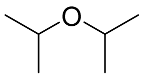
Only charged species appear in the mass spectrum of a compound. Choice (A) is an uncharged radical. Peaks for the positively-charged species (B), (C), and (D) can be seen at m/z 31, 56, and 84, respectively.

Where you've seen it: Fall 2015 Quiz $^{\#}$5 Problem I-6.

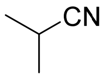
(18) A The IR spectrum below corresponds to which of the following compounds?



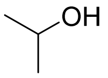
Source: Spectral Database for Organic Compounds, diisopropyl ether, #2837
http://sdbs.db.aist.go.jp/



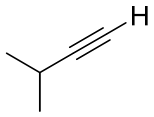
(A)



(B)



(C)



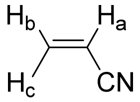
(D)

Sometimes the absence of peaks is just as telling as the presence of peaks. There are no significant stretching absorptions in this spectrum except for C(*sp*^{3})-H stretching. Stretching absorptions for C≡N, O–H, and C(sp)–H are absent. Therefore, the most obvious choice is (A).

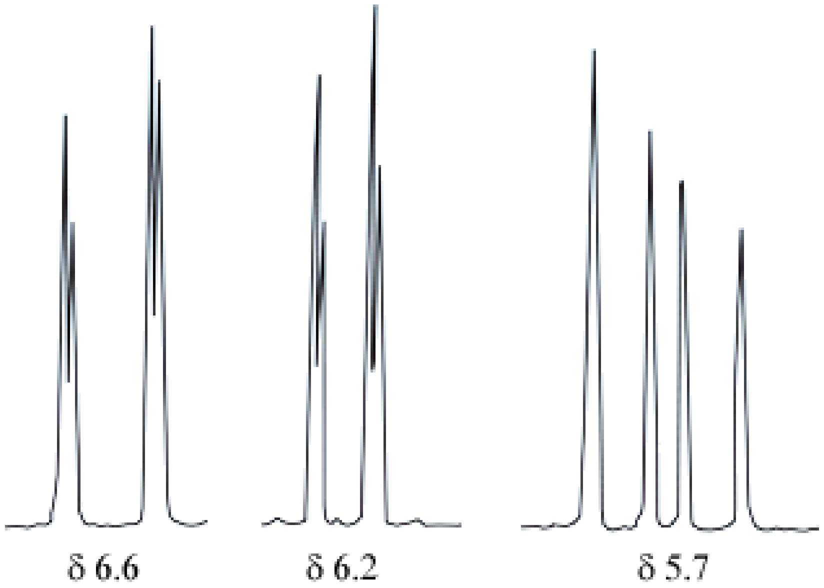
Where you've seen it: Summer 2016 Quiz $^{\#}$4 Problem I-7.

(19) A

Signals from the ^{1}H NMR spectrum of acrylonitrile (**R**) are shown below. Which signal corresponds to the H_a proton? The coupling constants are J_{ab} = 11.8, J_{ac} = 18.0 Hz, J_{bc} = 0.9 Hz. Assume the scale of the x-axis is the same for each peak.



R



Adapted from: Organic Chemistry, 5th edition, by Janice G. Smith

(A) the resonance for the H_a proton is at δ 5.7 ppm
(B) the resonance for the H_a proton is at δ 6.2 ppm
(C) the resonance for the H_a proton is at δ 6.6 ppm
(D) insert amusing incorrect answer here that the students will all enjoy, and hopefully, not pick.

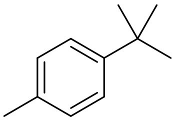
The coupling constants control the spacing between the daughter peaks in each split signal. The relatively large values of J_{ab} and J_{ac} suggest the signal for the H_a proton will be spaced out. The small value of J_{bc} suggests the close spacing of the split daughter peaks for H_b and H_c.

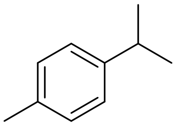
Where you've seen it: Smith textbook, Chapter 14 Problem 45 and Connect.

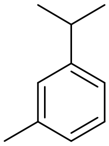
(20) B Which of the following compounds is consistent with the ^{1}H NMR spectral data given below?

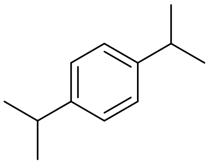
Chemical Shift (ppm)	**Multiplicity**	**Integration**
7.14	doublet	4
7.07	doublet	4
2.92	septet	2
2.46	singlet	6
1.32	doublet	12

Source: Computer simulation


(A)


(B)

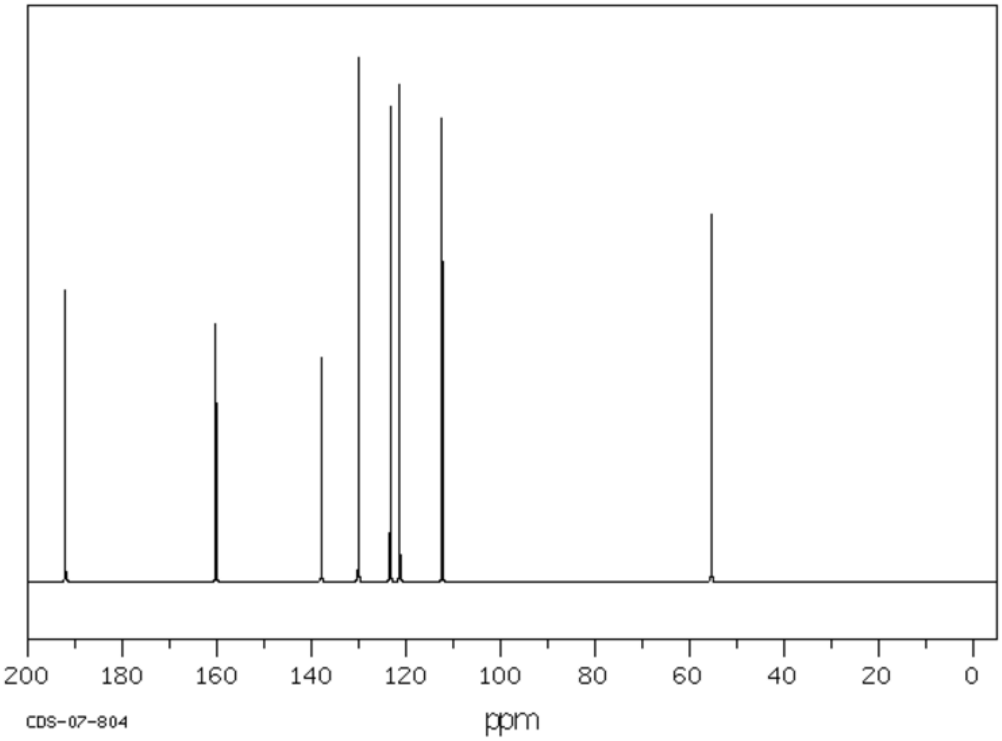

(C)


(D)

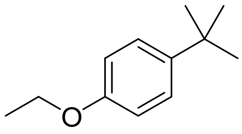
The aromatic doublet/doublet pair suggests 1,4-substitution. The septet/doublet upfield signals suggest an isopropyl group, while the 3H signal suggests a methyl group.

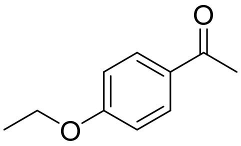
Where you've seen it: various ^{1}H NMR spectroscopy problems worked in class

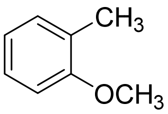
(21) D Which of the following compounds is consistent with the proton-decoupled ^{13}C NMR spectrum shown below? (Note: all peaks are singlets.)



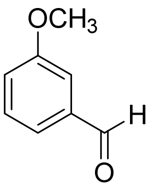
Source: Spectral Database for Organic Compounds, *m*-methoxybenzaldehyde, #1678
http://sdbs.db.aist.go.jp/


(A)


(B)



(C)

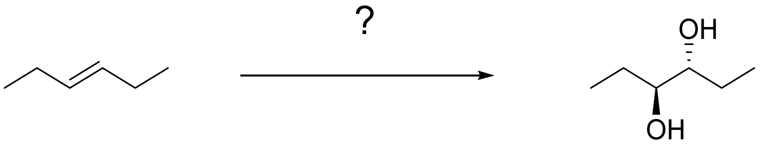


(D)

The upfield signal suggests a carbonyl group. The downfield signal suggests a carbon bonded to an electronegative atom like oxygen. The six central signals suggest an asymmetrically substituted benzene ring.

Where you've seen it: various ^{13}C NMR spectroscopy problems worked on various old exams.

(22) ____D____ Which of the following sequences will carry out the conversion of **S** to **T**?



S **T**

(A) 1. OsO_4; 2. $NaHSO_3$, H_2O
(B) 1. mCPBA; 2. catalytic H_2SO_4, H_2O
(C) 1. mCPBA; 2. catalytic NaOH, H_2O
(D) both (B) and (C) will carry out this conversion

Symmetrical, *trans*-alkenes (e.g., **S**) will afford a pair of enantiomers as products upon dihydroxylation with syn addition (e.g., by use of osmium tetroxide). Symmetrical, *trans*-alkenes will afford a meso product (e.g., **T**) upon dihydroxylation with anti addition (e.g., by epoxidation followed by hydrolysis in either acid or base).

Where you've seen it: This exact same question appeared on Fall 2016 Exam #3 (Problem I-22)!

(23) ____D____ If the year in which Lancastrian King Henry V won decisive victory over the French at the Battle of Agincourt were an IR absorption in units of cm^{-1}, which of the following modes would most likely correlate to the absorption?

(A) N–H stretching
(B) C=O stretching
(C) C≡N stretching
(D) CH_2 bending

Note: This question is just for kicks. Any answer, including leaving it blank, will not affect your score. But we did promise in lecture to ask about the Battle of Agincourt…

The Battle of Agincourt took place in 1415. All of the stretching frequencies listed are too energetic to correspond to this absorption.

Where you've seen it: such a question was suggested in Fall 2016 lecture and discussion of the St. Crispin's Day speech by Henry V.

Problem II. Explanation (4 points). Greenhouse gases absorb IR radiation and trap heat in our atmosphere. This process is necessary for our existence—without it, the Earth would cool too rapidly. The enhanced greenhouse effect occurs when molecules are added to our atmosphere that causes it to be too hot. The main gases that compose our troposphere are nitrogen, oxygen, carbon dioxide, water vapor, and argon. Circle below which of these gases in our atmosphere are greenhouse gases and explain what physical property makes them greenhouse gases in one sentence.

Circle the greenhouse gases: N_2 O_2 [✓ CO_2] [✓ H_2O] Ar

One-sentence explanation:

Only CO_2 and H_2O have bond stretches that are IR active (result in a change in dipole moment upon vibration).

Where you've seen it: slides and discussion for IR-active compounds in Chapter 13.

Grading and partial credit:

+2 points: CO_2 and H_2O are circled, along with no incorrect answers
+1 point: H_2O and/or CO_2 is circled, along with one or fewer incorrect answers
+0 points: Neither CO_2 nor H_2O is circled or they are circled but so are two or more incorrect answers

+2 points: full credit if the explanation discusses changes in dipole moment at all
+1 point: any other mention of dipole moment
+1 point: mention of "IR active" without mention of dipole moments

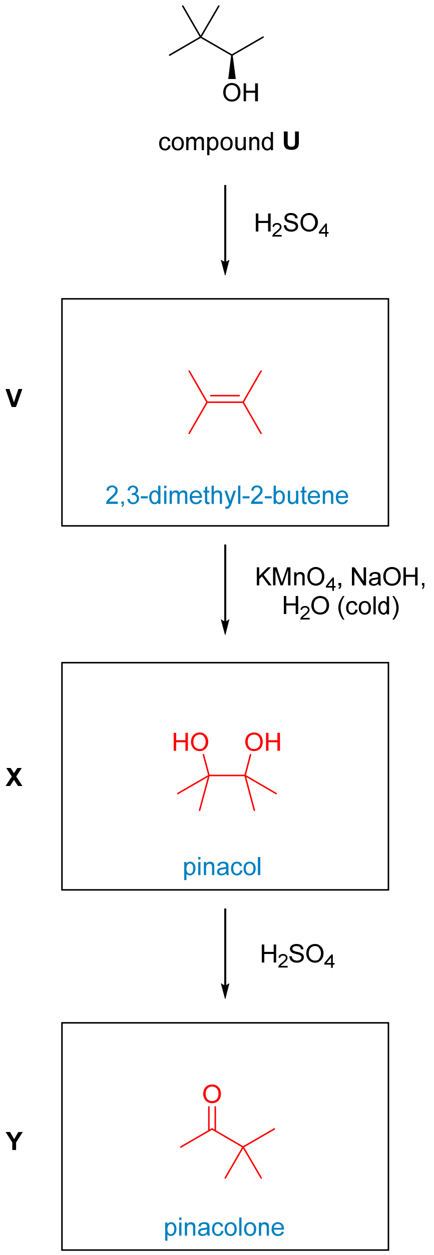
Problem III. (9 points) Roadmap Problem. Provide structures for compounds **V**, **X**, and **Y** consistent with the information provided below.

Compound **U** is the alcohol drawn below. Treatment of **U** with sulfuric acid in the absence of water yields compound **V** as a product that distills out of the reaction mixture. Compound **V** displays no strong, broad absorption in the IR around 3300 cm^{-1} and no significant absorption near 1700 cm^{-1}. Its electron-impact mass spectrum has a molecular ion peak at m/z 84. Treatment of **V** with cold, dilute, basic potassium permanganate yields **X** as the major product. Compound **X** has an intense, broad absorption in the IR around 3300 cm^{-1}. Its ^{1}H NMR spectrum has two signals: δ 2.40, 1.23, with an integration ratio of 1:6. When **X** is treated with a catalytic amount of sulfuric acid, it is converted to compound **Y** in high yield. **Y** has a molecular ion of m/z 100. Its ^{1}H NMR spectrum has two signals and its ^{13}C NMR spectrum has four signals. The IR spectrum for **Y** has a strong absorption at 1710 cm^{-1}, but no significant peaks above 3000 cm^{-1}.

Source: Spectral Database for Organic Compounds (2,3-dimethyl-2-butene, #4816; pinacol, #10089; 3,3-dimethyl-2-butanone, #1790)
http://sdbs.db.aist.go.jp/

Compounds & Reactions

Pertinent Spectral Data for Associated Compound

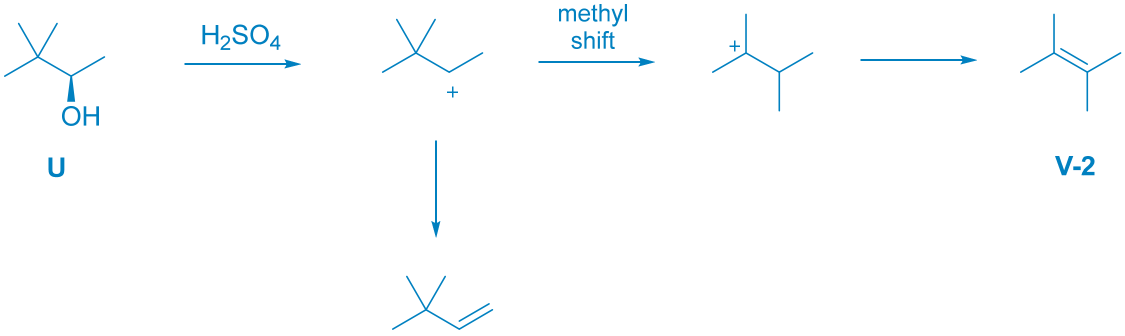


- Electron-impact MS has M$^+$ peak of m/z 84
- Does not have IR absorption band near 1700 cm^{-1}
- Does not have the strong, broad IR absorption around 3300 cm^{-1}
- ^{1}H NMR spectrum has one signal, at δ 1.64
- ^{13}C NMR spectrum has two signals: δ 123, 20

- Intense, broad IR absorption near 3300 cm^{-1}
- ^{1}H NMR spectrum has two signals: δ 2.40, 1.23 with an integration ratio of 1:6

- Electron-impact MS has M$^+$ peak of m/z 100
- Strong IR absorption at 1710 cm^{-1}
- No strong absorptions above 3000 cm^{-1}
- ^{1}H NMR spectrum has two signals
- ^{13}C NMR spectrum has four signals: δ 214, 44, 26, 25

The best way to work this problem—or any roadmap—is to start from the position where you have the most information. Here, that is at the start, since you have the exact structure of compound **U**. **U** has a molecular mass of 102 a.m.u. Note that the molecular mass of **V** is 84 a.m.u., reflecting a loss of 18 a.m.u. This mass and the treatment of an alcohol (**U**) with anhydrous H_2SO_4 suggests that **V** is produced from the loss of water from **U**. Perhaps the most obvious product to try first is **V-1**:



U

V-2

V-1

But if we look at the given spectroscopy data, we see that **V-1** has too many ^{1}H NMR signals and too many ^{13}C NMR signals. We need to be looking for something with more symmetry. So, if we go back to the carbocation intermediate expected from **U**, can we do anything else? Yes: a methyl shift to generate a more-stable carbocation that will lead to the formation of candidate structure **V-2**. Candidate **V-2** does match the given spectroscopy data.

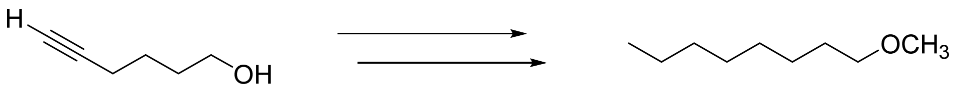
Mercifully, the reaction from **V** to **X** is straightforward dihydroxylation. The conversion of **X** to **Y** must be accompanied by the loss of both OH groups and the appearance of a carbonyl group, based on the IR data. **X** is set up perfectly for a pinacol rearrangement—heck, **X** is actually pinacol—to form ketone **Y**. If you're having trouble recognizing this rearrangement right off the bat, again, you should look at the difference in mass of **X** and **Y** (18 a.m.u.) to suggest the loss of water, and the use of sulfuric acid suggests the reaction should proceed by a carbocation intermediate, which you should then be suspicious of rearrangement to more-stable cations.

Where you've seen it: <u>very similar</u> to Fall 2015 Quiz $^{\#}$4 Problem III (elimination of water with rearrangement → dihydroxylation pinacol rearrangement) except that problem offered no spectral data to assist solving the structures. A spectroscopy roadmap problem with a carbocation rearrangement as also worked as an in-class problem in Fall 2016 Lecture 38.

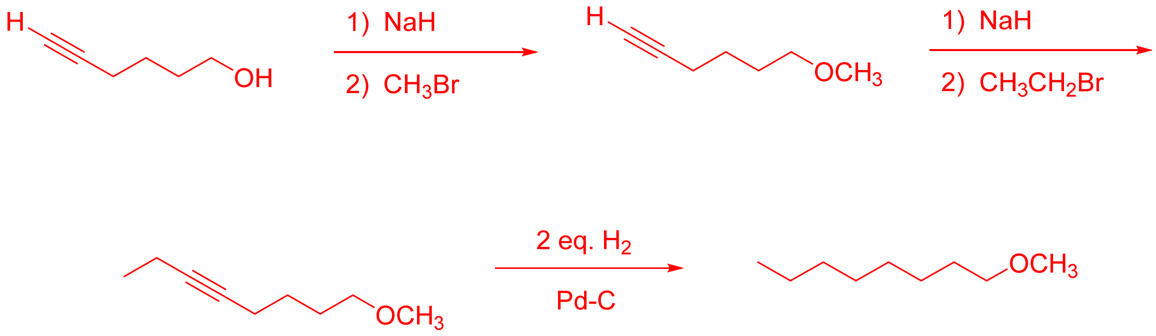
Grading and partial credit:

+3 points:	for each correct answer
+1 point:	**V** is *tert*-butylethylene (elimination without carbocation migration)
+0.5 point:	**V** is not *tert*-butylethylene, but it has no OH group and no carbonyl group
+1 point:	**V** was an incorrect alkene but **X** is the correct dihydroxlylation product
+0.5 points:	else, **X** has at least one OH group
+0.5 points:	**Y** has a carbonyl group and no OH groups

Problem IV. Synthesis (9 points). Provide a synthetic route—i.e, a sequence of reactions—to produce 1-methoxyoctane (**AA**) from 5-hexyne-1-ol (**Z**) and any other starting materials or reagents you need that contain three carbon atoms or fewer.



Z **AA**



The first thing to notice is that the product has two extra carbons in the hydrocarbon chain relative to the starting material and that the OH group seems to be converted to a methoxy group. At this point in the semester, the only way we know how to add multiple carbon atoms to the hydrocarbon chain is by alkylation of acetylide ions. Fortunately, the starting material is set up perfectly for this reaction. We also know we can alkylate alcohols to make ethers by the Williamson ether synthesis.

We have to deal with the proton on the hydroxyl group first because it is more acidic than the proton on the terminal alkyne. Thus, we must take care of methylating the oxygen prior to ethylating the alkyne/acetylide. The last step to finish off the synthesis is to hydrogenate the π bonds of the alkyne to produce the uninterrupted alkyl chain. The hydrogenation must be completed after the alkylation of the acetylide.

Where you've seen it: Fall 2015 Exam #3 Problem V, this synthesis is very similar to many found in old exams and in examples worked in class and at CYOA this year; almost exactly like Fall 2014 Hour Exam $^{\#}$3 Problem V except shorter/easier; very similar to Fall 2016 CYOA 10/24+25 session; very similar to Fall 2016 Lecture 31 Slide 11 in-class problem.

Grading and partial credit:

full credit	synthesis matches key or uses any other alkyl halides or tosylates (not just bromo)
+6 total	all correct except student generates and alkylates the acetylide before installing the methoxy group

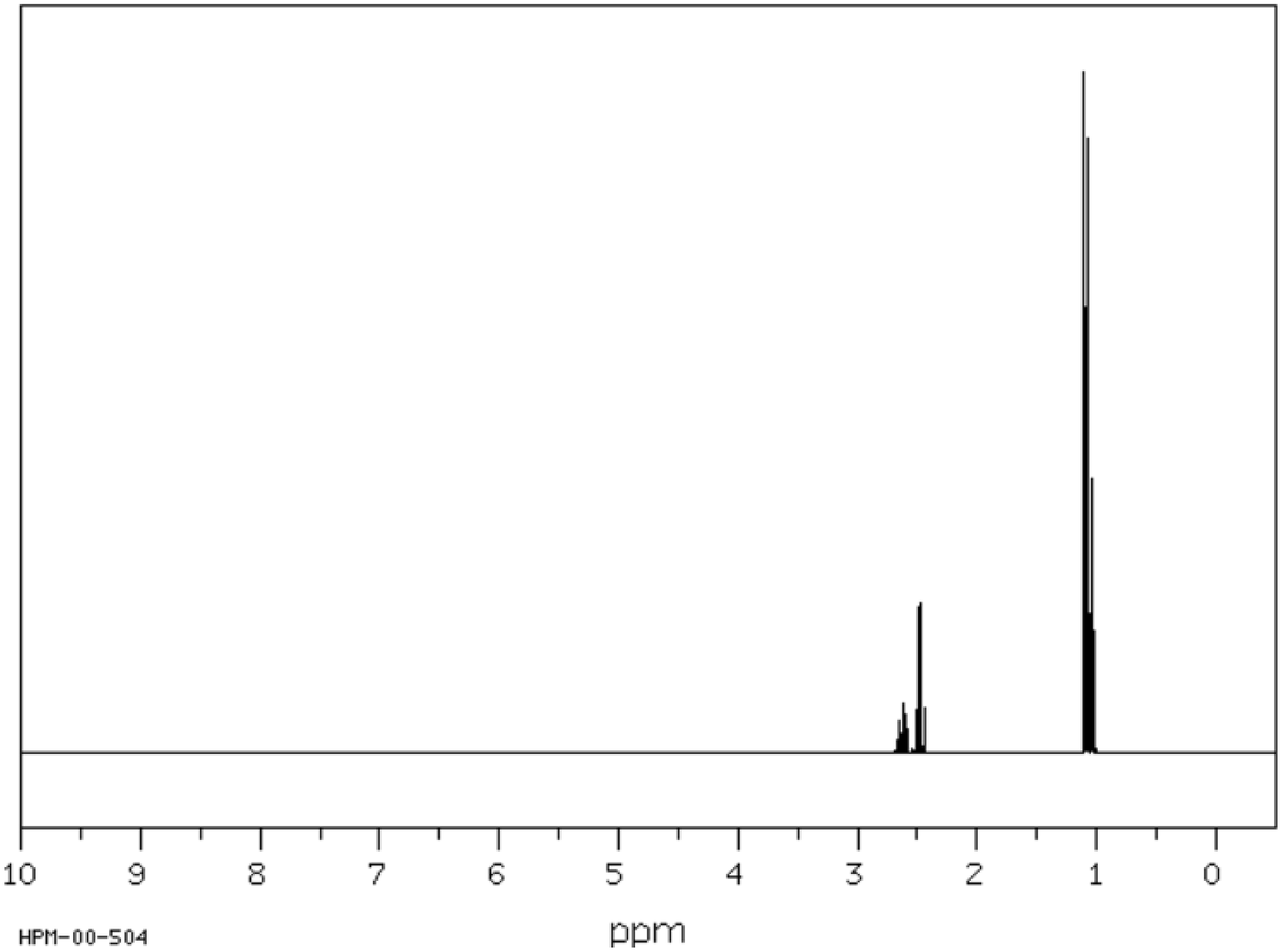
Small errors (give full credit then subtract points for the following):

−2 points	student omits base to deprotonate acetylide
−1 point	student uses a base that is too weak (e.g., NaOH)
−1 point	alkyl halide is missing a carbon or has one extra carbon (each)
−0 points	student installs methoxy group by tosylation or conversion to halide followed by methoxide attack (let it slide, though it introduces the possibility of elimination and is not ideal for Williamson ether synthesis)
−1 point	student forgets to write H_2 or Pd-C for hydrogenation, but has the other

Charity partial credit (start at zero and add points for each of the following):

+1 point	synthesis is a loss, but charity for any attempt at alkylation of acetylide
+1 point	synthesis is a loss, but charity for any attempt at alkylation of the oxygen or substitution by methoxide or methanol to install the methoxy group
+1 point	synthesis is a loss, but charity for any attempt at hydrogenation of the alkyne

Problem V. Assignment of an NMR Spectrum (12 points). High-resolution mass spectral analysis of a pure sample of compound **BB** reveals it to have a molecular formula of $C_6H_{12}O$. The ^1H NMR spectrum of **BB** in $CDCl_3$ has the following signals:



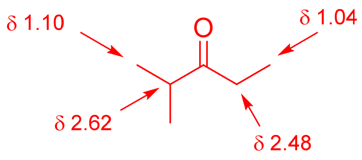
Source: Spectral Database for Organic Compounds, 2-methyl-3-pentanone, #23514
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Integration
2.62	septet	6
2.48	quartet	11
1.10	doublet	37
1.04	triplet	19

In the space provided on your official answer sheet:

(i) (4 points) Draw a Lewis structure for compound **BB** consistent with the data provided above.

(ii) (8 points) For each chemical shift, draw an arrow pointing to one of the hydrogens that gives rise to that signal.



BB

2-methyl-3-pentanone

Chemical Shift (ppm)	**Multiplicity**	**Integration**
2.62	septet	6
2.48	quartet	11
1.10	doublet	37
1.04	triplet	19

Where you've seen it: Many in-class examples and problems on old spectroscopy exams.

Grading and partial credit:

Structure:

+4 total	the structure is correct

Partial credit:

+1	the structure has molecular formula $C_6H_{12}O$
+1	the structure has an isopropyl group
+1	the structure has an ethyl group

Assignment (start at zero and add points for all of following):

+1	arrow points to a hydrogen that reasonably has the given chemical shift for whatever structure is drawn
+1	arrow points to a hydrogen that matches the given multiplicity, for whatever structure is drawn

Please Make Sure to Do the Following After Completing Your Exam

1. Ensure that all of your selected circles are darkened completely.

2. Submit your answer sheet, exam booklet, and scratch paper to the proctors. You may not remove these items from the exam room.

3. Turn in your note sheet with your name and Banner ID written clearly in the appropriate space. Your note sheet will be returned to you on Monday.

Scratch Paper

You may rip this sheet out of the exam booklet, but you are responsible for turning it in at the end of the exam.

Exam Booklet No.