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)	
Student Signature	

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

This exam focuses on Chapters 12, 13, and 14 in Janice Smith's *Organic Chemistry*, 4th ed.

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) _____ Which of the following statements is correct?

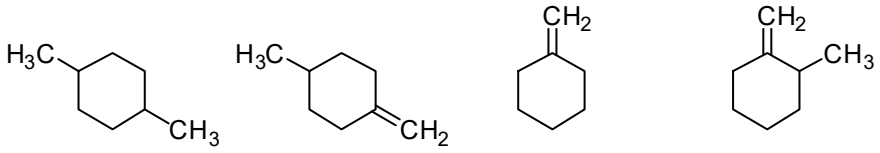
(A) a compound with a chemical shift of 7.20 ppm collected on a 300 MHz NMR spectrometer will also have a chemical shift of 7.20 ppm on a 700 MHz spectrometer

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

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

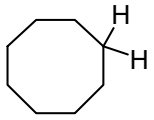
(D) the alignment of nuclear spin <u>against</u> an external magnetic field is lower-in-energy than alignment <u>with</u> the external magnetic field

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



(A) (B) (C) (D)

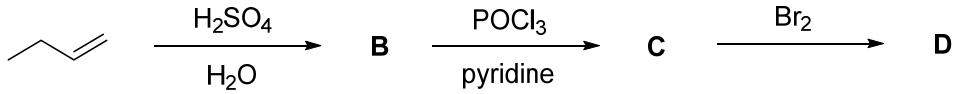
(3) _____ Two of the sixteen hydrogen atoms in compound **A**, cyclooctane, are drawn explicitly below. What is the multiplicity of the signal corresponding to the drawn hydrogen atoms?



A

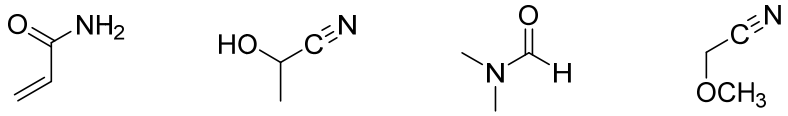
(A) singlet
(B) doublet
(C) triplet
(D) triplet of triplets

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



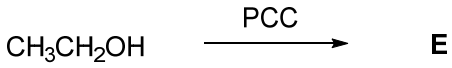
(A) (B) (C) (D)

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

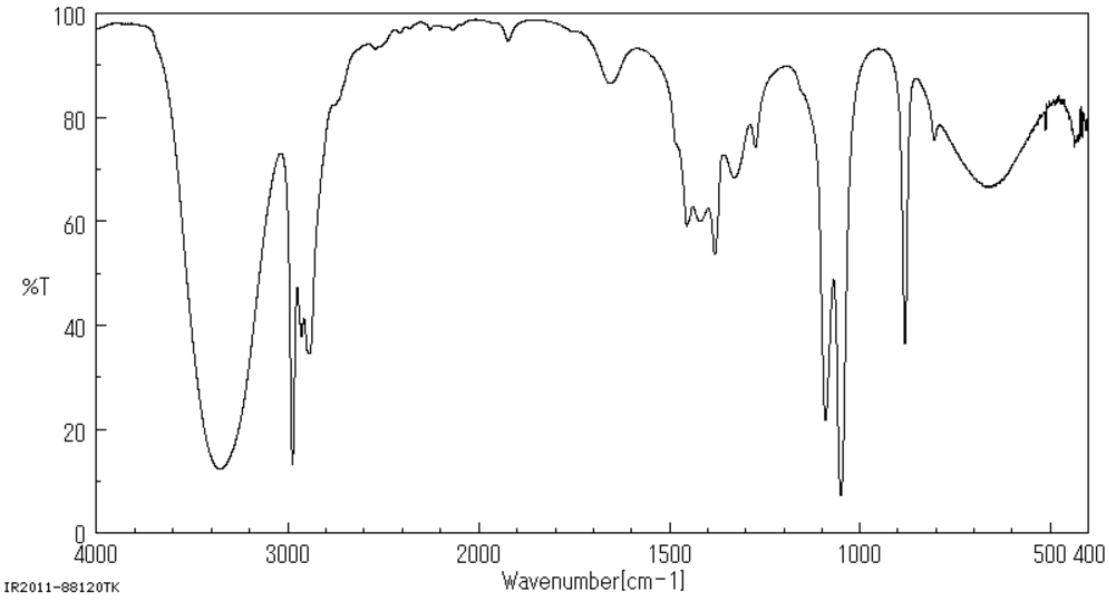


(A) (B) (C) (D)

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



IR Spectrum of ethanol:



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

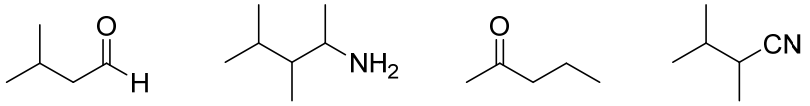
Source: Spectral Database for Organic Compounds, #305
http://sdbs.db.aist.go.jp/

(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}

(7) _____ 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?

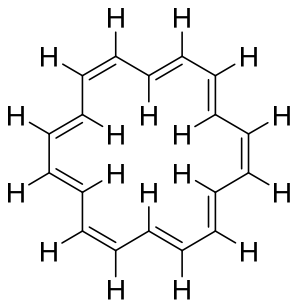
(A) $C_6H_8O_3$
(B) $C_7H_{12}O_2$
(C) $C_8H_{16}O$
(D) $C_6H_{15}N_3$

(8) _____ 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)

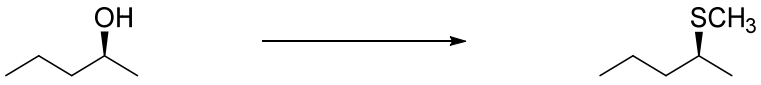
(9) _____ Compound **F** is 18-annulene, an aromatic compound with 18 π electrons, has a similar response to benzene in the presence of an applied magnetic field. The ^{1}H NMR spectrum of **F** has two signals: δ 8.9 ppm and δ −1.8 ppm. Which of the following statements is <u>not</u> true of compound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

(10) _____ Which of the following sequences of reactions is the best choice to convert **G** to **H**?



G **H**

(A) PBr_3 → $NaSCH_3$, DMSO

(B) TsCl, pyridine → $NaSCH_3$, DMSO

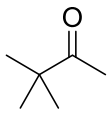
(C) H_2SO_4, H_2O → CH_3SH, H_2SO_4

(D) $SOCl_2$ → CH_3SH, H_2SO_4

(11) _____ Which of the following compounds will have the <u>most</u> signals in its ^1H NMR spectrum?

(A) (B) (C) (D)

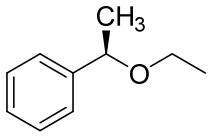
(12) _____ Which set of m/z values below represents significant peaks in the electron-impact mass spectrum of compound **J**?



J

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

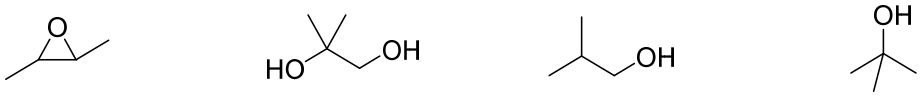
(13) _____ How many signals (arising from sets of inequivalent protons) appear in the ^{1}H NMR spectrum of compound **K**. Hint: Be careful!



K

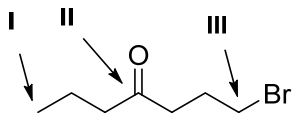
(A) 6 signals
(B) 7 signals
(C) 8 signals
(D) 9 signals

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



(A) (B) (C) (D)

(15) _____ 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**.

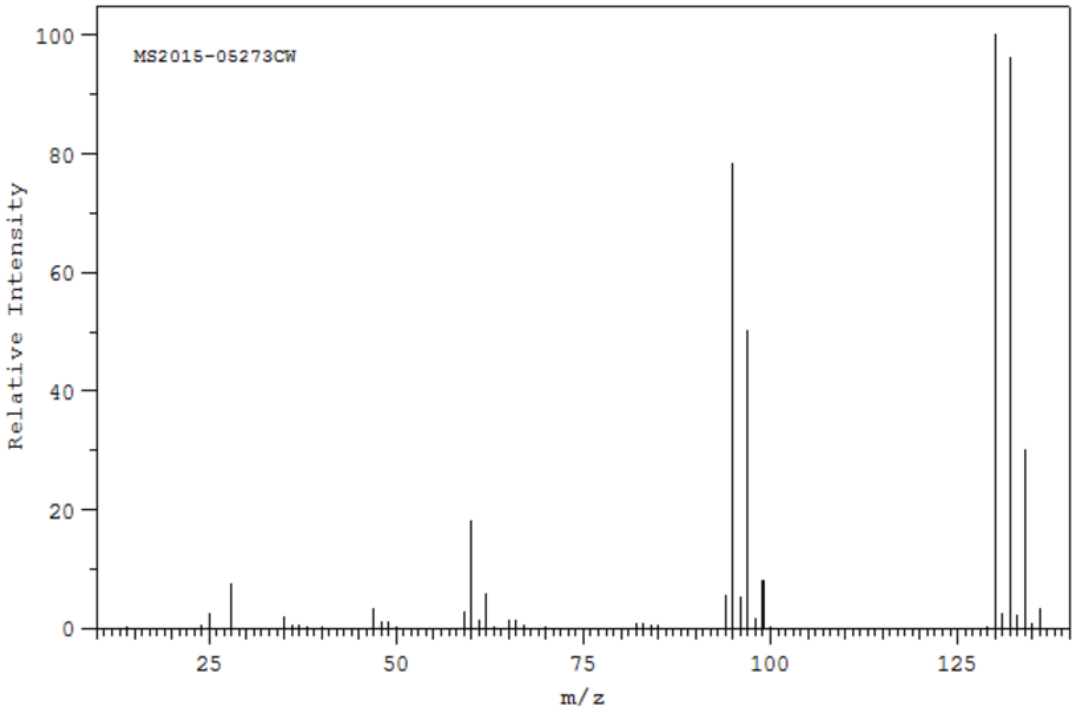


N

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

(16) _____ 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**:

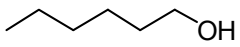


Source: Spectral Database for Organic Compounds, #2151
http://sdbs.db.aist.go.jp/

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

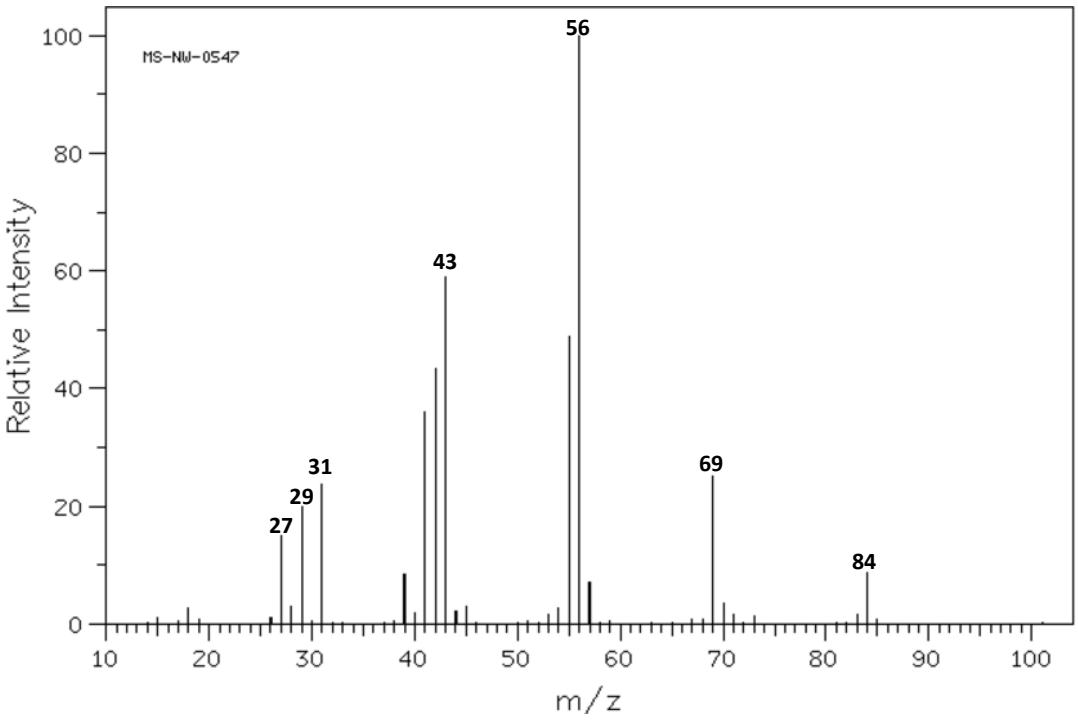
(A) one chlorine atom
(B) two chlorine atoms
(C) three chlorine atoms
(D) four chlorine atoms

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

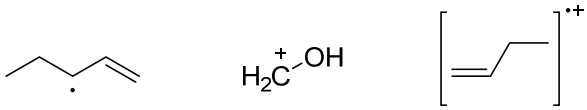


Q

EI Mass Spectrum of Compound **Q**:

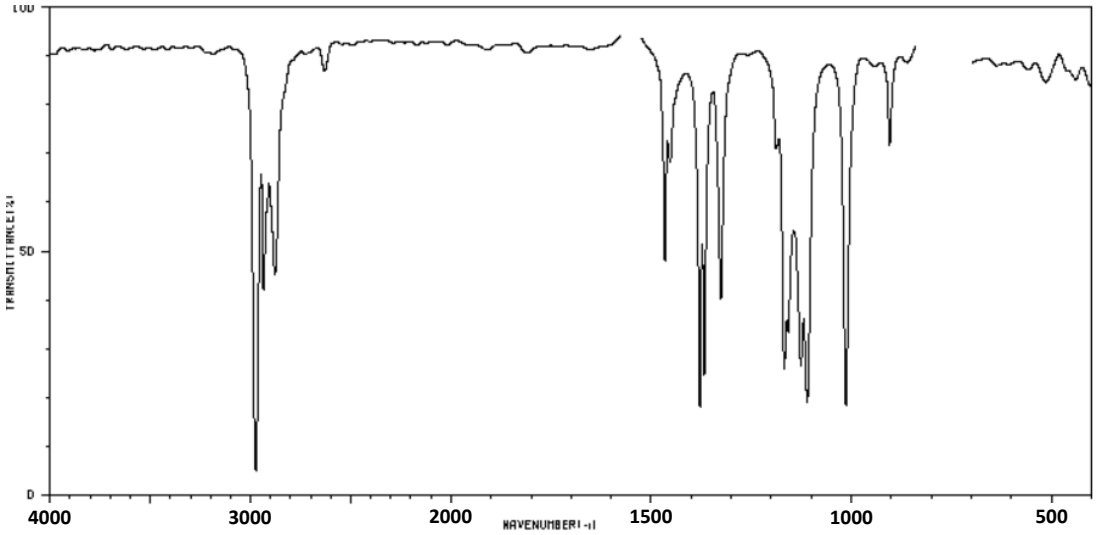


Source: Spectral Database for Organic Compounds, #1303
http://sdbs.db.aist.go.jp/



(A) (B) (C) (D)

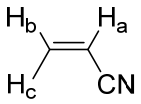
(18) _____ The IR spectrum below corresponds to which of the following compounds?



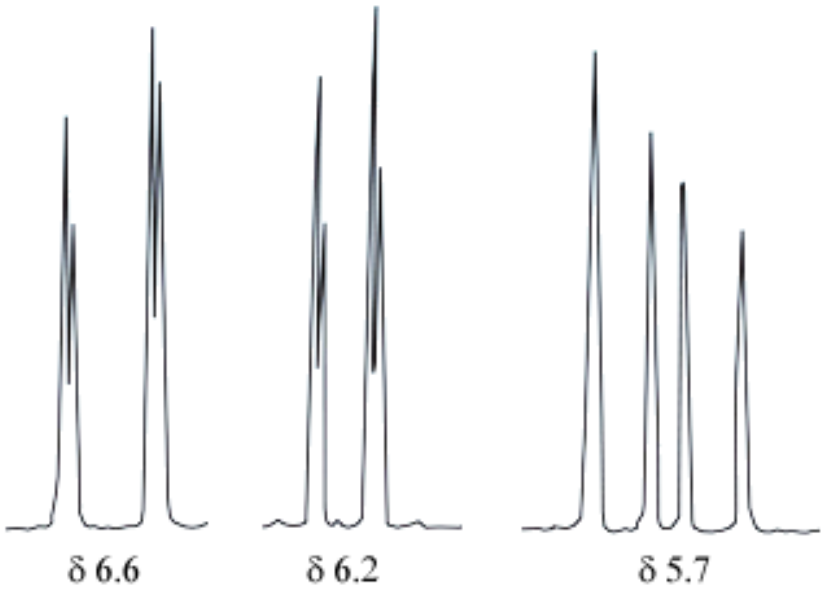
Source: Spectral Database for Organic Compounds, #2837
http://sdbs.db.aist.go.jp/

(A) (B) (C) (D)

(19) _____ 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



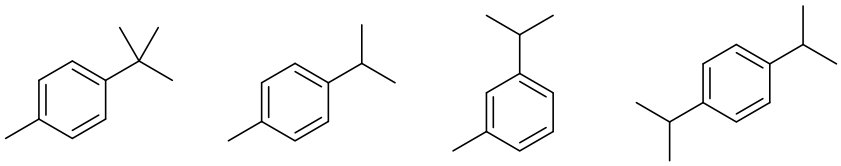
Adapted from: Organic Chemistry, 5th edition, by Janice G. Smith

(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.

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

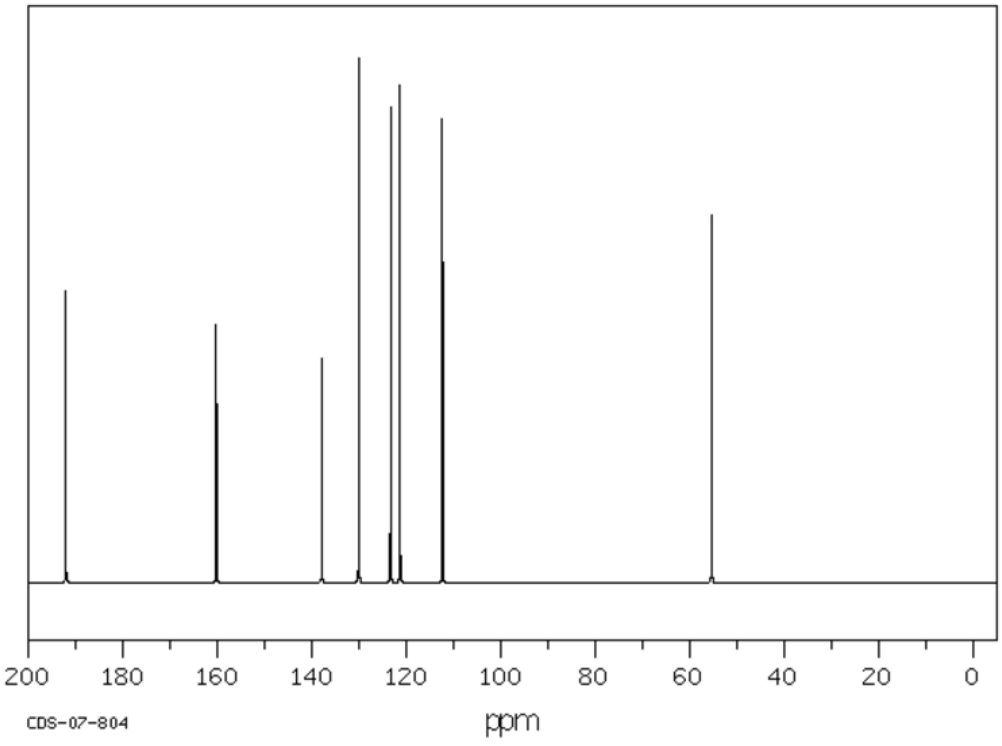
Chemical Shift (ppm)	Multiplicity	Integration
7.14	doublet	4
7.07	doublet	4
2.92	septet	2
2.46	singlet	6
1.32	doublet	12

Source: Computer simulation

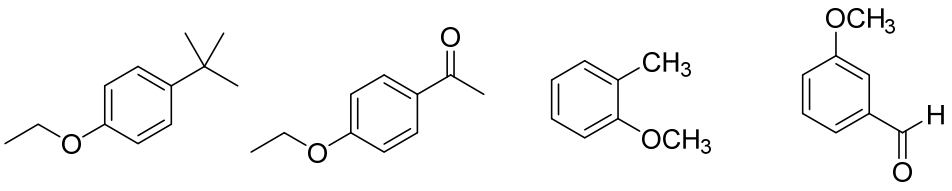


(A) (B) (C) (D)

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

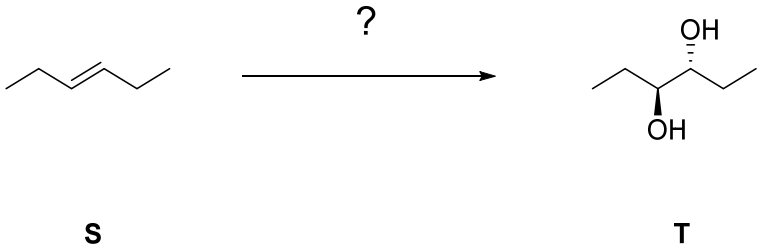


Source: Spectral Database for Organic Compounds, #1678
http://sdbs.db.aist.go.jp/



(A) (B) (C) (D)

(22) _____ 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

(23) _____ 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…

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.

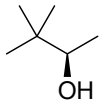
Circle the greenhouse gases: N_2 O_2 CO_2 H_2O Ar

One-sentence explanation:

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}.

<u>Compounds & Reactions</u> <u>Pertinent Spectral Data for Associated Compound</u>



compound **U**

H_2SO_4

V

- Electron-impact MS has M^+ peak of m/z 84
- Does <u>not</u> have IR absorption band near 1700 cm^{-1}
- Does <u>not</u> 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

$KMnO_4$, NaOH, H_2O (cold)

X

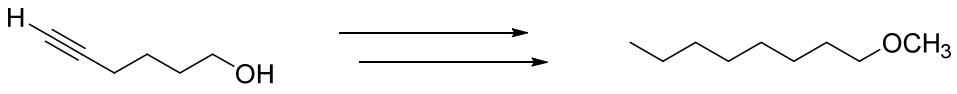
- Intense, broad IR absorption near 3300 cm^{-1}
- ^{1}H NMR spectrum has two signals: δ 2.40, 1.23 with an integration ratio of 1:6

H_2SO_4

Y

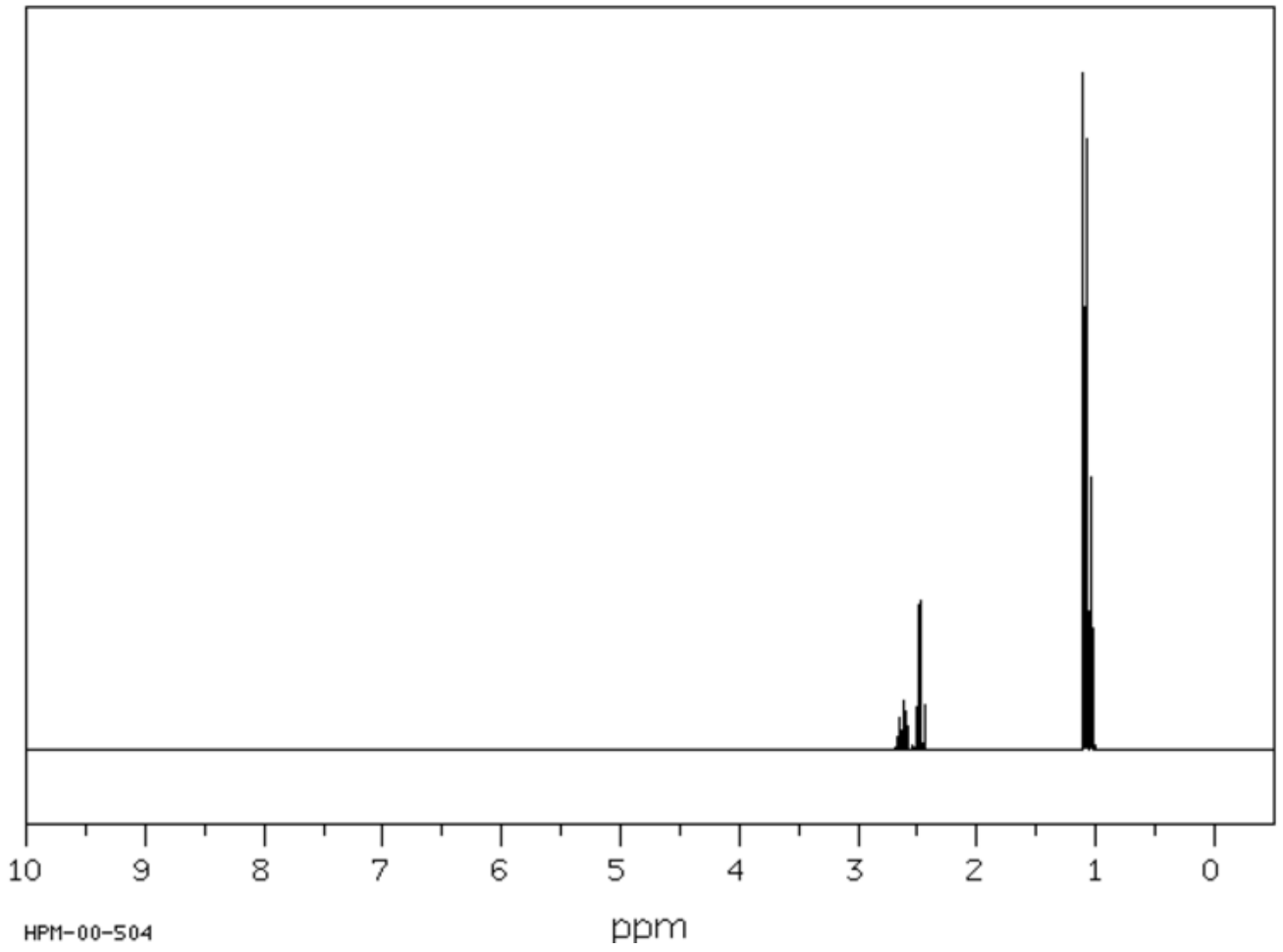
- Electron-impact MS has M^+ peak of m/z 100
- Strong IR absorption at 1710 cm^{-1}
- No strong absorptions above 3000 cm^{-1}
- ^{1}H NMR spectrum has two signals
- ^{13}C NMR spectrum has four signals: δ 214, 44, 26, 25

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**

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, #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.

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.