

CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Final Examination

Friday, December 11th, 2015

12:00–1:50 p.m. in Macelwane Hall 342

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

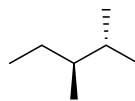
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		40
II		16
III		18
IV		10
V		16
TOTAL		100

Questions, **Required Information**, **Supplementary Information**

Problem I. Multiple choice (40 points total; +4 points for a correct answer, +1 point for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

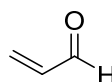
- (1) E Which of the following statements is not correct regarding compound **A**?



A

- (a) compound **A** has 16 hydrogen atoms
- (b) compound **A** has at least one primary, secondary, and tertiary carbon
- (c) compound **A** is named (*S*)-2,3-dimethylpentane
- (d) compound **A** is an isomer of 2,2,3-trimethylbutane
- (e) compound **A** has a higher boiling point than heptane (a.k.a., *n*-heptane)

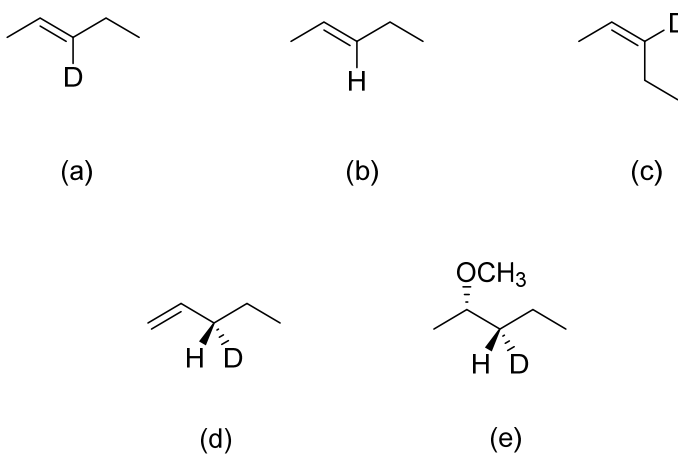
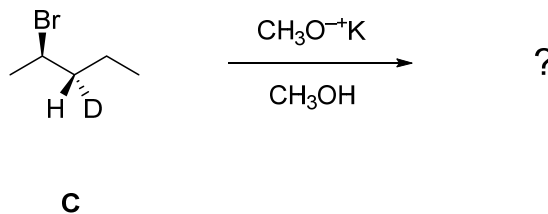
- (2) B Which of the following types of orbitals is not involved in forming a bond in compound **B**?



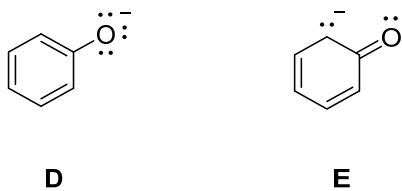
B

- (a) an sp^2 -hybridized orbital on carbon
- (b) an sp^3 -hybridized orbital on carbon
- (c) an unhybridized p orbital on carbon
- (d) an unhybridized p orbital on oxygen
- (e) an unhybridized s orbital on hydrogen

- (3) ^A Which of the compounds below is not expected to be a significant product when compound **C** is treated with potassium methoxide in methanol?

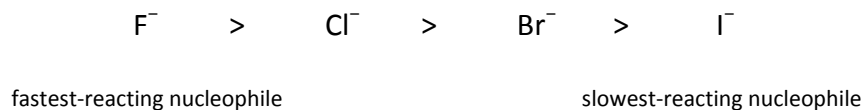


- (4) ^A What is the relationship of Lewis structures **D** and **E**, shown below?



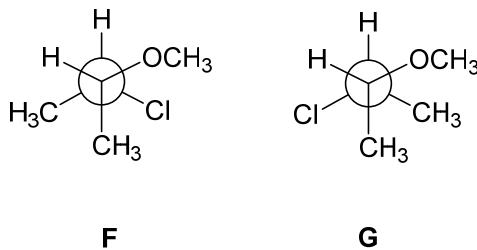
- (a) resonance forms
 (b) tautomers
 (c) enantiomers
 (d) diastereomers
 (e) an acid/conjugate base pair

- (5) A For an S_N2 reaction, under what circumstances is the following trend in nucleophilicity generally true?



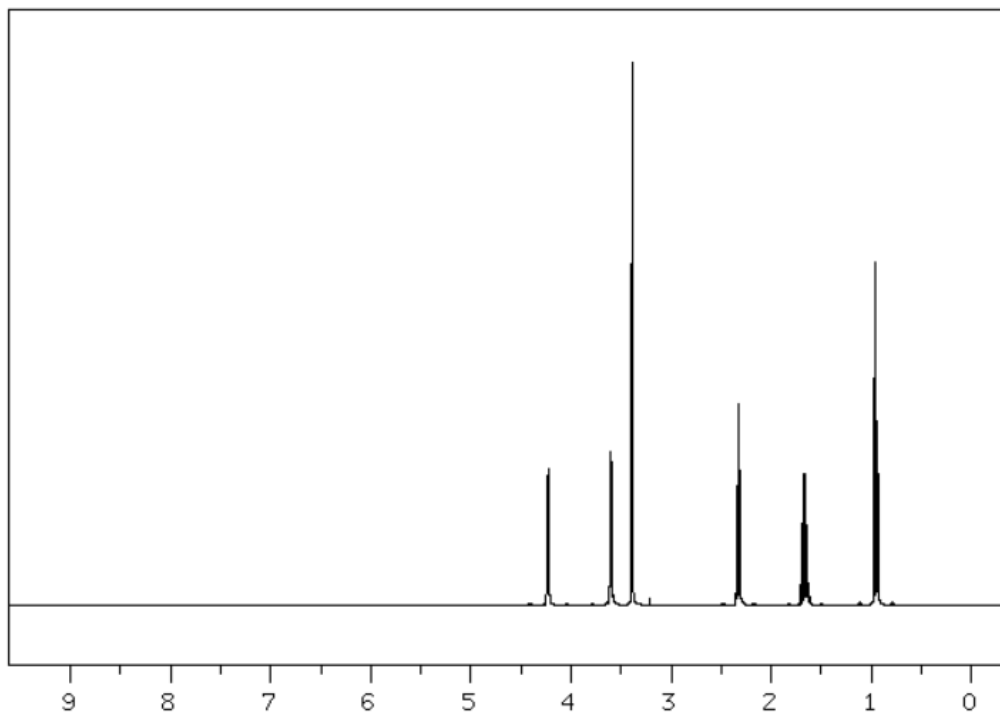
- (a) in polar, aprotic solvents like DMSO
- (b) in polar, protic solvents like methanol
- (c) in both aprotic and protic solvents
- (d) in neither aprotic nor protic solvents

- (6) C What term best describes the relationship of the molecules drawn below as Newman projections **F** and **G**?



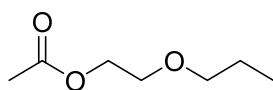
- (a) identical compounds
- (b) stereoisomers with the exact same melting point
- (c) stereoisomers with different melting points
- (d) structural/constitutional isomers
- (e) conformational isomers

(7) D The ^1H NMR spectrum shown below corresponds to what compound?

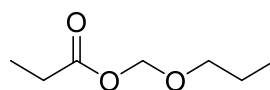


Source: Spectral Database for Organic Compounds, #17070
<http://sdbs.db.aist.go.jp/>

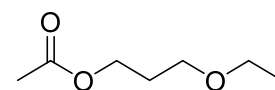
Chemical Shift (ppm)	Multiplicity	Integration
4.23	triplet	41
3.60	triplet	40
3.39	singlet	62
2.33	triplet	42
1.66	multiplet	39
0.95	triplet	61



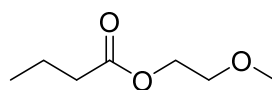
(a)



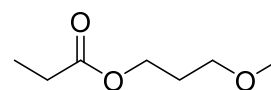
(b)



(c)

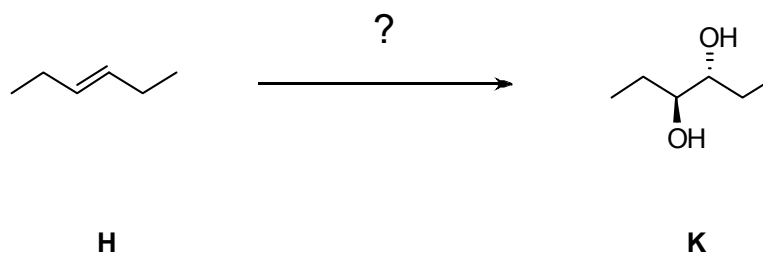


(d)



(e)

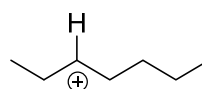
- (8) D Which of the following stepwise reactions will carry out the conversion of **H** to **K**?



- (a) 1. OsO₄; 2. NaHSO₃, H₂O
 (b) 1. mCPBA; 2. H₃O⁺
 (c) 1. mCPBA; 2. NaOH, H₂O
 (d) both (b) and (c) will carry out this conversion
 (e) (a), (b), and (c) will all carry out this conversion

Symmetrical, *trans*-alkenes (e.g., **H**) will afford a meso product (e.g., **K**) upon dihydroxylation with anti addition (e.g., by epoxidation followed by hydrolysis, which can be catalyzed with either acid or base). Symmetrical, *trans*-alkenes will afford a pair of enantiomers as products upon dihydroxylation with syn addition (e.g., by use of osmium tetroxide). Symmetrical, *cis*-alkenes will afford a pair of enantiomers as products upon dihydroxylation with anti addition. Symmetrical, *cis*-alkenes will afford a meso product upon dihydroxylation with syn addition.

- (9) E Which of the following statements most completely and correctly describes carbocation **M**?

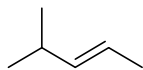
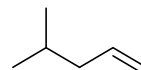


M

- (a) **M** can be formed by heterolytic cleavage of the C–Cl bond in 3-chloroheptane
 (b) **M** is a secondary carbocation
 (c) **M** is stabilized by the overlap of filled C–H and C–C σ bonding orbitals with the empty unhybridized p orbital on carbon
 (d) both (a) and (b) are true
 (e) (a), (b), and (c) are all true

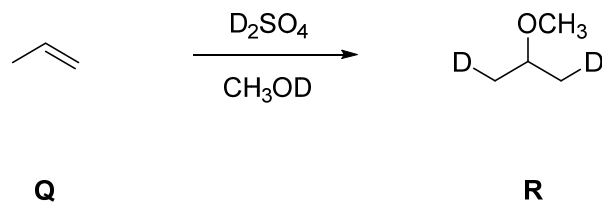
(10) ^B

Which of the following statements is true and most complete in its comparison of compounds **N** and **P**?

**N****P**

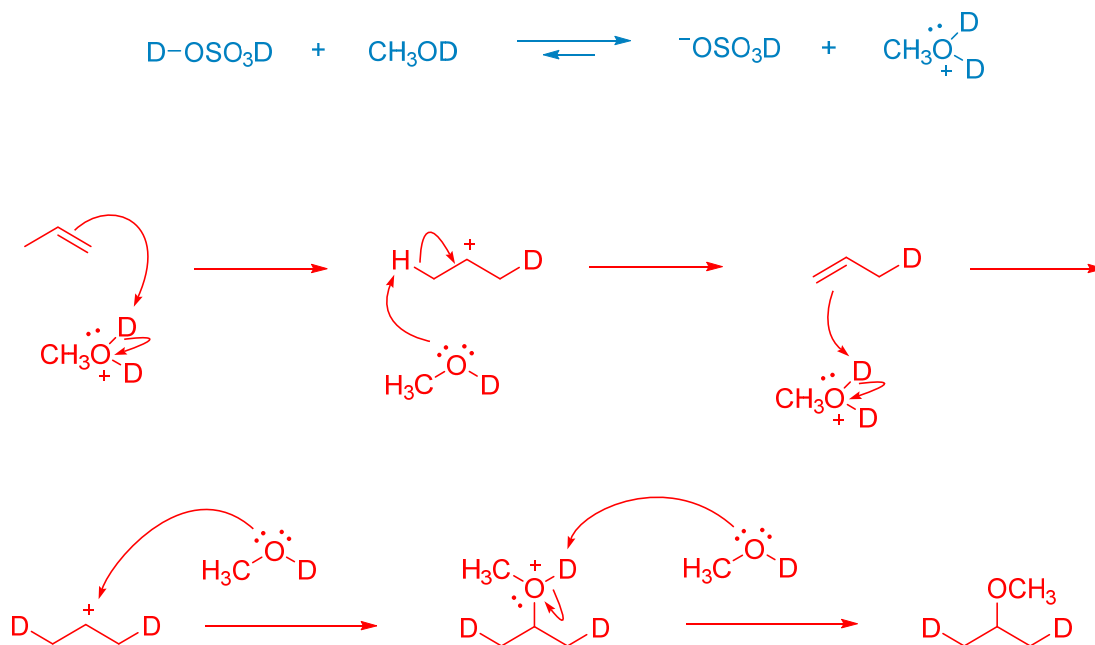
- (a) compound **N** and **P** are diastereomers
- (b) compound **N** has a less exothermic heat of hydrogenation than **P**
- (c) compound **N** has a faster rate of hydrogenation on Pd-C than **P**
- (d) statements (b) and (c) are both true
- (e) statements (a), (b), and (c) are all true

Problem II. Mechanism (16 points). Draw a sensible mechanism for the following reaction. Remember to use proper “curved arrow notation” to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the resonance. Show all significant resonance forms that account for the stability of the intermediates in the reaction.



Notes:

- Compound **R** is not the major product of this reaction
- Remember, D = ^2H (an isotope of hydrogen)

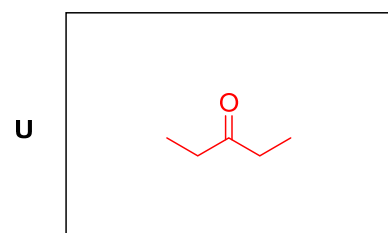
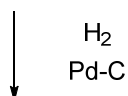
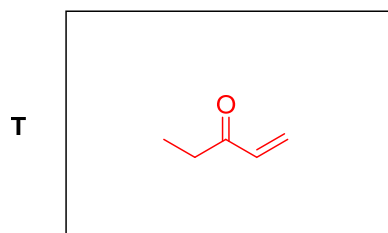
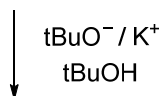
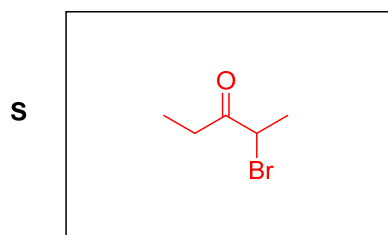


Note that the second step is just the first step in reverse, but from the other side of the molecule.

Problem III. (18 points) Roadmap Problem. Provide structures for compounds **S**, **T**, and **U** given the information listed below.

Compound **S** has a strong absorption in its IR spectrum not too far above 1700 cm^{-1} . Its electron-impact mass spectrum has a molecular ion split into two peaks: 164 and 166 m/z . The relative ratio of the intensities of these peaks is roughly 1:1. The ^1H NMR spectrum of **S** has four signals: a doublet, a triplet, and two quartets. When **S** is treated with potassium *tert*-butoxide, compound **T** is the major product. High-resolution mass spectrometry of **T** reveals it to have a molecular formula of $\text{C}_5\text{H}_8\text{O}$. The peak in the IR spectrum described above for compound **S** is shifted to 1685 cm^{-1} for compound **T**. When **T** is exposed to 1 equivalent of hydrogen gas and palladium fixed to a carbon substrate, the major product is **U**. The ^1H NMR spectrum of **U** has just two signals: δ 2.44 (quartet) and 1.06 (triplet). The integrations of these peaks have a relative ratio of 2:3. The ^{13}C NMR spectrum of **U** has three signals.

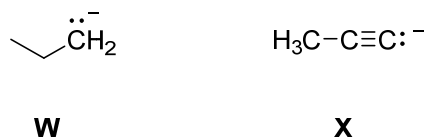
Compounds & Reactions



Pertinent Spectral Data for Associated Compound

- IR spectrum has strong absorption just above 1700 cm^{-1}
 - M^+ peak split into 164 and 166 m/z in approximate 1:1 ratio
 - ^1H NMR spectrum has 4 signals: a doublet, triplet, and two quartets
-
- High-resolution MS gives a molecular formula of $\text{C}_5\text{H}_8\text{O}$
 - IR spectrum has strong absorption at 1685 cm^{-1}
-
- ^{13}C NMR spectrum has 3 signals
 - ^1H NMR spectrum in has two signals: δ 2.44 (quartet) and 1.06 (triplet) in a relative ratio of 2:3

Problem IV. Explanations (10 points). Of compounds **W** and **X**, which is the stronger base? Briefly explain why. Please begin your answer with the sentence “Compound ___ is the stronger base.”



Compound **W** is the stronger base. The lone pair on **X** is in an orbital with more *s*-character (*sp* vs. *sp*³ for **W**). Electron density in orbitals with higher *s*-character is positioned closer to the nucleus, where it is less available to serve as a base. It makes sense that **X** is the weaker base because its conjugate acid is a stronger acid ($pK_a \approx 25$ vs. a $pK_a \approx 50$ for the conjugate acid of **W**).

Problem V. Synthesis (16 points). Provide a synthetic route—i.e, a sequence of reactions—to produce heptanal (**Z**) from 1-pentanol (**Y**) and any other reagents you wish.

