**YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM**

- PRINT YOUR NAME ON EACH PAGE!
- WRITE CLEARLY!
- READ THE DIRECTIONS CAREFULLY!
- MOLECULAR MODELS ARE ALLOWED
- USE BLANK PAGES AS SCRATCH PAPER
- DO NOT USE RED INK
- work on blank pages will not be graded...
- DON'T CHEAT, USE COMMON SENSE!

<table>
<thead>
<tr>
<th>Interaction Energies, kcal/mol</th>
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<tbody>
<tr>
<td>Eclipsing</td>
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<tr>
<td>H/H</td>
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<td>H/Me</td>
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<tr>
<td>Me/Me</td>
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<td>t-Bu/Me</td>
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</tbody>
</table>

**Infrared Correlation Chart**

- broad $\sim$3300
- broad with spikes $\sim$3300
- broad $\sim$3000
- range of values
- $\delta$ (ppm)
- cm$^{-1}$

**NMR Correlation Charts**

- Alkyl
- Aromatic
- main ring $\delta$ - 6.5
- 3' > 2' > 1'
- 3' > 2' > 1'
- variable and condition dependent, ca. 2 - 6 $\delta$
- R$\to$H variable and condition dependent

- PRINTED FIRST NAME ____________ Answer ____________ PRINTED LAST NAME ____________ Key ____________

Person on your LEFT (or Empty or Aisle) ____________

Person on your RIGHT (or Empty or Aisle) ____________

Class you are REGISTERED FOR (onground or hybrid) ____________

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid)

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YOU MUST COMPLETE THIS PAGE WITH YOUR NAME
(EVEN THOUGH YOU ALREADY DID THIS ON THE COVER PAGE)
AND ALSO GIVE YOUR ASU OR POSTING ID NUMBER
WE NEED THIS NUMBER BECAUSE YOU WOULDN'T BELIEVE THE NUMBER OF
STUDENTS WHOSE NAMES WE CAN'T READ!

Points by question

1___________/14
2___________/20
3___________/28
4___________/34
5___________/30
6___________/30
7___________/20
8___________/63
9___________/24
10___________/30
11___________/16
12___________/20
13___________/20
14___________/26

Points Removed for cover errors ___/2

Extra Credit_____/5

Total (incl Extra)______/175+5

**YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM**
Question 1 (14 pts.) Give the IUPAC name for the following. Specify stereochemistry as appropriate.

(6R)-chloro-(5S)-methyl-3-phenyl-(2Z)-heptene

Question 3 (28 pts) Give a curved arrow mechanism for the following reaction. Label the Lewis and Bronsted acid/base for each intermolecular step. **GIVE THE NUMBER OF SETS OF INTERMEDIATES AND THE NUMBER OF TRANSITION STATES for your mechanism.**

# of transition states ____________
# of sets of intermediates ____________

Question 12 (20 pts.) For the following two structures, assign absolute configuration (R or S) to all chiral (asymmetric) centers, state whether the two structures are a pair of enantiomers, a pair of diastereomers or the same thing drawn two different ways, and identify any meso compounds.
Question 4 (34 pts.).

a) Give a curved arrow mechanism for the following reaction. Where appropriate, label the Lewis acid and Lewis base in each step, and whether they are also Brønsted acids and bases, include all resonance contributors as appropriate. 

**clearly indicate the rate determining step!!**

b) Draw a properly labelled reaction energy diagram for this reaction and on the diagram...

1. indicate the positions of each of the intermediates
2. include the positions of the transition states but do NOT draw any transition states
3. Clearly indicate the activation energy for every mechanistic step, and clearly indicate the rate determining step
4. Clearly indicate the reaction exothermicity
Question 5 (30 pts) For (3R)-bromo-(4S)-methylhexane:

a) Draw a 3-D structure for the **lowest energy conformation**

b) Draw a Newman projection for the conformation that can undergo E2 elimination

c) Draw the transition state for E2 elimination using $\text{Na}^+ - \text{O-t-Bu}$ as the base

d) Give the E2 elimination product

![3D reactant](image1)

![Newman](image2)

![E2 transition state](image3)

![E2 product](image4)

Question 6 (30 pts) For the structure shown below

a) Draw the **lowest energy chair conformation**

b) Draw the chair conformation that can undergo E2 elimination

c) Draw the transition state for E2 elimination using $\text{Na}^+ - \text{O-t-Bu}$ as the base

d) Give the E2 elimination product

![lowest energy chair](image5)

![E2 chair](image6)

![E2 transition state](image7)

![E2 product](image8)

Question 7 (20 pts.). Indicate whether you would expect each reaction to be SN1, SN2, E1 or E2 and give the major organic product(s), paying attention to all possible stereoisomers. State whether a solution of the product(s) would be optically active and give a brief justification.

a) Allylic chloride, strong base/nucleophile BUT E2 not possible, must be SN2

![allylic chloride](image9)

b) Allylic bromide, weak base/nucleophile BUT E2 not possible, must be SN1

![allylic bromide](image10)
Question 8 (63 pts.) Give the missing major ORGANIC PRODUCT for each reaction.

a) Show all stereochemistry as appropriate, identify any MESO compounds.

b) Briefly explain whether and why a solution of the product would be optically active or not.

c) Assign each reaction as addition, elimination, substitution or rearrangement.

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a)  
\[ \text{NBS} \quad \text{hv} \quad \text{Br} \quad \text{not optically active, racemic} \]

b)  
\[ \text{Ph} \quad \text{Br} \quad \text{CCl}_4 \quad \text{addition not optically active, meso} \]

c)  
\[ \text{1. H}_2\text{O/Hg(OAc)}_2 \quad \text{2. NaBH}_4 \quad \text{not optically active, achiral} \]

d)  
\[ \text{K}^+ \text{O-t-Bu acetone} \quad \text{elimination not optically active, achiral} \]

e)  
\[ \text{1. BH}_3\text{THF} \quad \text{2. H}_2\text{O}_2/\text{HO} \quad \text{addition not optically active, racemic} \]

f)  
\[ \text{MeOH boil} \quad \text{elimination not optically active, achiral} \]

(give the elimination product)

g)  
\[ \text{1 Equiv. Na}^+\text{OMe DMF} \quad \text{not optically active, achiral} \]
Question 9 (24 pts.) Assign the following reactions as SN1, SN2, E1 or E2 and give a brief explanation for your choice. Draw an energy diagram with properly labelled axes for both reactions ON THE SAME DIAGRAM (assume both are exothermic). Normalize your energy diagrams at the transition states. Include the activation energy for both reactions on the diagram. Explain which reaction will be faster and give a brief explanation that includes the term "energy of the electrons".

these are substitution reactions, the nucleophile is a strong nucleophile $\text{-OMe}$, the mechanism must be SN2.

the nucleophile anion and the leaving group anion are more highly solvated in the polar protic solvent MeOH in A compared to the polar aprotic solvent acetone in B, solvation lowers the energy of the electrons in the anions, decreasing reactivity, reaction B is thus faster.

Extra Credit (5 pts.) Which of the following drugs resulted in terrible birth defects in Europe in the 1960s?

ibuprofen  thalidomide  ketamine  thebaine
Question 10 (30 pts.) For the following Bronsted acid/base reaction (not all H atoms are included in the provided structures)

a) Label the **STRONGER** acid/base and the **WEAKER** acid/base on EACH side

b) Indicate which reaction would be faster, left to right or right to left

c) Indicate on which side the equilibrium will lie

d) Indicate which acid has the smaller and which the larger pKa

e) Give a BRIEF explanation for your choice of stronger/weaker Bronsted acids/bases that includes drawings of ALL relevant resonance contributors

f) Give a reaction energy diagram that includes the activation energy for reaction in BOTH directions

g) draw the transition state for the reaction

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**Diagram**

- **Stronger acid**
  - ![Structure](image1)
  - Energy: $E_a \overset{L>R}{=}$ left to right
  - $L>R$ = right to left

- **Stronger base**
  - ![Structure](image2)
  - Energy: $E_a \overset{R>L}{=}$ right to left

- **Weaker acid**
  - ![Structure](image3)
  - ![Structure](image4)

- **Weaker base**
  - ![Structure](image5)

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**Explanation**

- The stronger base has the higher energy electrons, that are least resonance stabilized.
- The weaker acid has the stronger conjugate base.
Question 11 (16 pts.) For the following compound, rank the pairs of electrons indicated as A, B, and C in order of INCREASING energy, give a BRIEF explanation.

- A (these nonbonding electrons)
- B (electrons in this π bond)
- C (electrons in this C–C σ bond)

Electrons A are non-bonding, electrons B are in a pi-bond, which has higher energy electrons than those in a sigma-bond, C.

Question 12 (20 pts.) For the localized molecular orbitals indicated, draw a picture of the Ψ or Ψ² as requested, directly ON TOP of the structures. In each case also give the atomic orbitals that are used to "build" the molecular orbitals. All non-bonding electrons are shown. Indicate the positions of any nodes for the Ψ. Indicate where the probability of finding the electrons is zero for the Ψ².

a) For the C–O π* orbital:
- Ψ
- Node
- C - p
- H
- H
- O - p

b) For the C–O σ orbital:
- Ψ
- Node
- C - sp
- H
- H
- O - sp²

Question 13 (20 pts). Classify the following reactions as substitution, elimination, addition or rearrangement. Which reaction would be faster? Give a BRIEF one-sentence explanation that includes the term "rate determining step" and "Hammond postulate".

A  Br

B  Br

These are SN1 reactions, weak nucleophile and polar protic solvent. The rate determining step is formation of a bromide anion and a cation. Reaction B forms a resonance stabilized cation in this SN1 reaction, which is more stable and requires less energy to form. The Hammond postulate says that the less endothermic reaction should have the smallest activation energy and be faster.
Question 14 (26 pts) Provided are spectra for a compound with molecular formula $C_5H_{12}O$

a) Give the degrees of unsaturation ________________

0 degrees of unsaturation

b) On the infrared spectrum, indicate which peaks correspond to which functional groups

[c] Draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum (only)