Extra Credit /5  Total (incl Extra) /375+5

**Chemistry 233, Fall 2012**

**Printed Name:**

**Printed Last Name:**

**ASU ID or Posting ID:**

**Person on your LEFT (or Aisle):**

1 /18  
2 /12  
3 /10  
4 /28  
5 /16  
6 /36  
7 /24  
8 /63

**Person on your RIGHT (or Aisle):**

9 /18  
10 /16  
11 /22  
12 /20  
13 /40  
14 /28  
15 /24  
16 /63

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**Chemical Elements:**

- H  Re
- Li  Be  B  C  N  O  F  Ne
- Na  Mg  Al  Si  P  S  Cl  Ar
- K  Ca  Sc  Ti  V  Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
- Rb  Sr  Y  Zr  Nb  Mo  Tc  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I  Xe
- Cs  Ba  Lu  Hf  Ta  W  Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  At  Rn

**Interaction Energies, kcal/mol:**

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<tbody>
<tr>
<td>H/H</td>
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<tr>
<td>H/Me</td>
<td>-1.4</td>
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<tr>
<td>Me/Me</td>
<td>-0.95</td>
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<tr>
<td>i-Pr/Me</td>
<td>-2.6</td>
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<tr>
<td>Me/1,3,5-TBu/Me</td>
<td>-2.9</td>
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**Infrared Correlation Chart:**

- **O-H**
- **N-H**
- **C=O**

**Approximate Coupling Constants, J (Hz), for ¹H NMR Spectra:**

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**NMR Correlation Charts:**

- **Alcohol (R-OH):**
  - Dependent, ca. 2 - 6 
- **Aromatic (R-C-H):**
  - mainly 8 - 6.5
- **Alkyl (R-C=CH):**
  - $3^\prime > 2^\prime > 1^\prime
- **Alkyl (R-C=CR):**
  - $3^\prime > 2^\prime > 1^\prime
- **HOC=CH (Alkyl):**
- **RC=CR (Aromatic):**
- **C-NR (Alkyl):**

**Aromatic C-H:**

<table>
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<th>(b, ppm)</th>
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**Common Sense Guidance:**

- **Print Your Name on Each Page!**
- **Read the Directions Carefully!**
- **Use Blank Pages as Scratch Paper**
- **Write Clearly!**
- **Molecular Models Are Allowed**
- **Do Not Use Red Ink**
- **Don’t Cheat, Use Common Sense!**
Question 1 (18 pts) Which of the indicated protons, Ha or Hb is more strongly Bronsted acidic? Give a BRIEF explanation, and support your explanation with drawings of the appropriate conjugate base anions.

![Chemical structure](image)

Question 2 (12 pts.) Give the IUPAC name for the following. Specify stereochemistry as appropriate.

![Chemical structure](image)

Question 3 (10 pts.)

a) What is the most important way in which a Lewis base is defined?

b) Which thermodynamic quantity is electron energy associated with?
Question 4 (28 pts.). For the following two reactions:
1) Add the curved arrow pushing and any relevant C-H bonds, and state the type of reaction (SN1/SN2/E1/E2), AND ADD THE MISSING OTHER PRODUCTS ON THE RIGHT HAND SIDE OF THE EQUATIONS
2) Indicate which would be faster and draw a reaction energy diagram for both on THE SAME DIAGRAM (normalize them at the transition states), draw arrows corresponding to the activation energies for each reaction and give a BRIEF explanation for your choice of faster and slower
3) Draw a picture of the transition state for (either of) the reaction(s)

A

B

Question 5 (16 pts)
a) Indicate which of the following two structures is the stronger Bronsted base, and give a brief explanation for your choice.

MeO⁻ MeS⁻

b) Indicate which of the following two structures A or B is the stronger Bronsted base, and give a brief explanation for your choice.

A

B
Question 6 (36 pts). For (1S)-bromo-(2S,3)-dimethyl-1-phenylbutane:

a) Draw a line-angle structure showing stereochemistry using wedged/dashed bonds

b) Draw a 3-D (sawhorse) structure AND a Newman projection for the lowest energy conformation for rotation around the C1-C2 bond

c) Draw a 3-D (sawhorse) structure AND a Newman projection for the conformation that is required for E2 elimination

d) Draw the E2 elimination product

\[
\begin{array}{c}
(1S)-\text{bromo-(2S,3)-dimethyl-1-phenylbutane} \\
\xrightarrow[\text{DMF}]{} \Theta \Theta \\
\text{Na} \\
\end{array}
\]

Line-angle structure, wedged/dashed bonds

\[
\begin{array}{c}
\text{E2 product} \\
d) \\
\text{line-angle structure} \\
\end{array}
\]

3D (sawhorse) AND Newman projection for lowest energy conformation

3D (sawhorse) AND Newman projection for E2 reactive conformation

Question 7 (24 pts). For the cyclohexane structure shown below, draw:

a) The **lowest energy chair conformation**

b) The **chair conformation** required for an E2 elimination reaction

c) The **product of an E2 elimination reaction**

\[
\begin{array}{c}
\text{Ph} \\
\text{Me} \\
\end{array}
\]

Br

\[
\begin{array}{c}
\text{lowest energy chair} \\
\text{chair for E2 elimination} \\
\text{E2 elimination product} \\
\end{array}
\]
Question 8 (63 pts.) For the following reactions:

a) Give the missing major ORGANIC PRODUCT

b) Show absolute and relative stereochemistry as appropriate, identify any MESO compounds

c) Briefly explain whether a solution of the product would be optically active and why or why not, simply stating that the reactant is achiral is insufficient for not optically active

a)  
\[
\begin{align*}
\text{Br}_2 & \quad \text{CCl}_4 \\
& \quad \text{products}
\end{align*}
\]

b)  
\[
\begin{align*}
\text{K}^+ & \quad \text{O-t-Bu} \\
\text{DMF} & \quad \text{products}
\end{align*}
\]

c)  
\[
\begin{align*}
\text{Excess HBr} & \quad \text{HOOH} \\
& \quad \text{products}
\end{align*}
\]

d)  
\[
\begin{align*}
1. \text{Hg(OAc)}_2 & \quad \text{H}_2\text{O} \\
2. \text{NaBH}_4 & \quad \text{products}
\end{align*}
\]

e)  
\[
\begin{align*}
\text{NBS} & \quad \text{hv} \\
& \quad \text{products}
\end{align*}
\]

f)  
\[
\begin{align*}
\text{H}_2/\text{Pd/C} & \quad \text{products}
\end{align*}
\]

g)  
\[
\begin{align*}
\text{EtOH} & \quad \text{heat} \\
& \quad \text{products}
\end{align*}
\]
Question 9 (18 pts.) For each reaction, decide whether the mechanism would be SN1/SN2/E1 or E2 and give a brief explanation. Draw the product and show stereochemistry where appropriate and state whether a solution of the product would be optically active or not AND give a BRIEF explanation.

a) 

b) 

Question 10 (16 pts.) For E1 elimination in the following structures (assume a polar protic solvent and heat), give the curved arrow pushing and the intermediates formed in FIRST STEP of the mechanism ONLY, include resonance contributors as appropriate. Rank the reactions A, B and C in order of increasing rate of E1 elimination, give a BRIEF explanation.

A 

B 

C 

\[ \text{slowest} < \quad < \quad \text{fastest} \]
Question 11 (22 pts.) For the following Bronsted acid/base reaction (not all H atoms are included in the provided structures)
a) Draw the curved-arrows that describe the bond making and breaking in BOTH directions
b) Label the STRONGER acid/base and the WEAKER acid/base on EACH side
c) Indicate which reaction would be faster, left to right or right to left
d) Indicate on which side the equilibrium will lie
e) Indicate which acid has the smaller and which the larger pKa
f) Give a BRIEF explanation for your choice of stronger/weaker Bronsted acids/bases that includes drawings of ALL relevant resonance contributors

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

Question 12 (20 pts.)
a) Draw a picture of the wavefunction, OR the wavefunction squared AS REQUESTED, for the molecular orbitals requested, on top the molecules. In each case indicate the A.O.'s used to make the M.O.'s.

\[
\begin{align*}
\psi^2 & \text{ for the C-C } \pi \text{ orbital} \\
\psi & \text{ for the C-Br } \sigma^* \text{ orbital}
\end{align*}
\]
Question 13 (40 pts) Reaction of HBr with both the cis- and the trans-isomers of the alkene below gives the same alkyl bromide product. Give a curved arrow mechanism for the reaction of the trans-isomer ONLY, where appropriate, label the Lewis acid and Lewis base in each step, and whether they are also Bronsted acids and bases. GIVE THE NUMBER OF SETS OF INTERMEDIATES AND THE NUMBER OF TRANSITION STATES that are associated with your mechanism.

\[
\begin{align*}
\text{ cis-alkene } & \quad \text{HBr} \quad :\text{Br} \quad \text{HBr} \quad \text{trans-alkene}
\end{align*}
\]

b) Draw a properly labelled reaction energy diagram for the reaction of the trans-isomer, clearly indicating the positions of the intermediates and draw structures for ALL of the transition states and indicate their positions on the diagram.

c) ADD the corresponding reaction energy diagram for the same reaction of the cis-isomer to your energy diagram above. Indicate, using arrows, the activation energies for the rate determining steps for BOTH reactions. BRIEFLY explain which isomer will react faster and why.
Question 14 (28 pts.) For the following reaction, give a full curved arrow mechanism, indicate the Lewis and Bronsted acids and bases at each step as appropriate. Do not draw transition state structures or an energy diagram, but state the number of sets of intermediates that are included in your mechanism and also how many transition states.

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

- ibuprofen
- thalidomide
- ketamine
- thebaine
Question 15 (24 pts) Provided are spectra for a compound with molecular formula $C_6H_{14}O$

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp$^3$)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific bond** in the functional that corresponds to the peak.

![Infrared spectrum]

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<tbody>
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ppm

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1H singlet
2H triplet
3H triplet
2H sextet
6H singlet


c) draw the structure and clearly indicate which hydrogens correspond to which signals in the **proton nmr spectrum (only)**