**INFORMATION**

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

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**CHEM 233, Fall 2017**

**Midterm #3**

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

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**Infrared Correlation Chart**

- **Interm Energies, kcal/mol**
  - **Eclipsing**
    - H/H: ~1.0
    - H/Me: ~1.4
    - Me/Me: ~2.6
    - Me/Me: ~0.9
    - Et/Me: ~0.95
    - i-Pr/Me: ~1.1
    - t-Bu/Me: ~2.7
  - **Gauche**
    - Et/Et: ~3.1

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**NMR Correlation Charts**

- **R—NH₂ variable and condition dependent, ca. 2 - 6 δ**
- **R—OH**
- **Aromatic**
- **Alkyl**
- **3' > 2' > 1'**

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**Chemical Elements**

- H, He, 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.
Question 1 (12 pts.) Give the IUPAC name for the following structure.

2-bromo-5,5-dimethyl-3-propyl-(2E)-hexene

Question 2 (35 pts.)

a) Give a full curved-arrow pushing mechanism for the following reaction, indicate the Lewis acid/base (LA/LB) and Bronsted acid/base (BA/BB) at each step as appropriate. **CLASSIFY THE OVERALL REACTION** as addition, elimination, substitution or rearrangement. **GIVE THE NUMBER OF transition states and the number of sets of intermediates in your mechanism.**

b) Draw a reaction energy diagram with properly labelled axes for the reaction above. **Draw on the diagram the activation energy for EVERY STEP of the mechanism, and clearly indicate which one is the rate determining step.** Also draw on the diagram the overall reaction exothermicity or endothermicity. Indicate the positions of the transition states (but do not draw the structures of the transition states).
Question 3 (30 pts)

a) For the reactions A and B, add the curved arrows that illustrate bond-making and bond-breaking, indicate the Lewis acids/bases (LA/LB) and whether they are also Bronsted acids/bases (BA/BB).

\[ \begin{align*}
\text{A} & \quad \text{H}_3\text{C}^- & \quad \text{B} & \quad \text{H}_3\text{C}^+ \\
\text{LA} & \quad \text{H} & \quad \text{LB} & \quad \text{H} \\
\text{B} & \quad \text{H}_3\text{C}^- & \quad \text{B} & \quad \text{H}_3\text{C}^+ \\
\text{LA} & \quad \text{H} & \quad \text{LB} & \quad \text{H}
\end{align*} \]

b) One of these reactions is exothermic, the other is endothermic. Decide which is which and give an explanation. Draw a reaction energy diagram for A and B ON THE SAME DIAGRAM (so that they can be compared, do not draw 2 different diagrams). Do not forget to properly label the axes and clearly indicate which diagram refers to which reaction!

reaction A is exothermic because it makes one sigma bond, no bonds are broken
reaction B is endothermic because it makes one sigma bond, breaks one sigma bond, but the negative charge goes from being on the electronegative oxygen to the non-electronegative boron

\[ \text{Energy} \]

\[ \begin{align*}
\text{E}_a^A & \quad \text{B} \end{align*} \]

\[ \text{reaction coordinate} \]

\[ \text{B endothermicity} \]

\[ \text{A exothermicity} \]

c) Indicate the activation energies for the two reactions on your energy diagram, and also indicate the exothermicity or endothermicity as appropriate. State which reaction, A or B would be FASTER, and BRIEFLY (one sentence) explain why.

reaction A is faster because it has a smaller activation energy because it is exothermic

d) Below, draw structures for the transition states for each reaction A and B.

\[ \begin{align*}
\text{A} & \quad \text{H}_3\text{C}^- & \quad \text{B} & \quad \text{H}_3\text{C}^+ \\
\text{LA} & \quad \text{H} & \quad \text{LB} & \quad \text{H} \\
\text{LA} & \quad \text{H} & \quad \text{LB} & \quad \text{H}
\end{align*} \]
Question 4 (24 pts.) Give the missing major organic products OR reagents/conditions as appropriate for each of the following reactions, include all non-bonding electrons. 

*clearly indicate stereochemistry in the products where relevant*

a) 

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{H}_2\text{SO}_4 \text{(cat.)} \\
\end{align*}
\]

b) 

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

c) 

\[
\begin{align*}
1. \text{BH}_3\text{-THF} & \quad 2. \text{HO/H}_2\text{O}_2 \\
\end{align*}
\]

Question 5 (20 pts.) The structure of aniline is shown below. Rank the carbon atoms labelled A, B and C in order of decreasing chemical shift in a 13C (carbon) nmr spectrum. You will need to draw minor resonance contributors in order to get the correct answer to this question. Give an explanation for your answer that includes the following terms, "electron density" and "shielding and/or deshielding" (you do not need to mention local magnetic field, although it will not be incorrect if you do).

\[
\begin{align*}
\text{NH}_2 & \quad \Theta \\
\end{align*}
\]

- C is most deshielded because it is attached to the electronegative nitrogen, it has the largest chemical shift

- The minor resonance contributors indicate that A has a partial negative charge, which increases electron density on this carbon, which increases shielding, or decreases deshielding, A has the smallest chemical shift

- C is closest to the electronegative N, it has the largest chemical shift

* A does not have the smallest chemical shift because it is farthest from the N, but that answer is worth partial credit
Question 6 (30pts.) For the following Bronsted acid/base equilibrium (not all of the H atoms are specifically shown in the line-angle structures):

a) Draw the curved arrows for reaction in both directions
b) Add any missing important resonance contributors for the anions on both sides of the equilibrium
c) Identify the stronger acid and base on each side, indicate which acid would have the smaller pKa, indicate which reaction would be faster and give a brief explanation for your choices
d) Indicate on which side the equilibrium would lie

Although both anions are resonance stabilized, the weaker base anion delocalizes the negative charge onto the more electronegative oxygen, lowering the electron energy, reducing the chemical reactivity of the electrons, the base is easier to make and thus has the stronger conjugate acid

e) Draw an energy diagram with properly labelled axes for the equilibrium shown above, showing the activation energy in BOTH directions, do NOT draw the transition state

Extra Credit (5 pts) Dr. Gould had a conversation with his daughter about which topic?

- cis- and saturated acids and Markovnikov
- trans- and unsaturated bases and Anti-Markovnikov
Question 7 (24 pts) Provided are spectra for a compound with molecular formula C₆H₁₂O₂

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate which peaks correspond to which functional groups (including C(sp³)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional group that corresponds to the peak.

![Infrared Spectrum]

C(sp³)-H: 3000-3600 cm⁻¹
C=O: 1600-1700 cm⁻¹
O-H: 3400 cm⁻¹

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

![Proton NMR Spectrum]

δ (ppm): 0.0-2.0
0.5-1.5: Methylenes
2.5-3.5: Methines
3.5-4.5: Methylene carbons
4.5-5.5: Olefinic carbons
5.5-6.5: Phenyl and aromatic carbons

Note: The spectrum shows two closely spaced peaks, indicating a hydrogen associated with a cis relationship to the oxygen.