A web search of 'chemistry cartoons' returned Sarah's anime elves. I think she did good work with entropy!

**Note:** Your exam should consist of 5 pages including the cover page and grade tabulation sheet. Skim the entire exam and solve the easiest problems first. Exams not returned at the end of the period will not be graded.

**PLEASE DO NOT OPEN THIS EXAM UNTIL YOU ARE INSTRUCTED TO DO SO**
1. Write conformational structures for the substitution products of the following deuterium-labeled compounds. 10 pts

\[
\begin{align*}
\text{Cl} & \quad \text{NaCN} \\
\text{H} & \quad \text{CH}_3\text{OH} \\
55 \, ^\circ \text{C} & \\
\text{D} & \quad \text{CH}_3\text{OH} \\
0 \, ^\circ \text{C} &
\end{align*}
\]

2. One of the two compounds shown below undergoes a reaction with methanol solvent at room temperature to form an optically active solution, while the other compound reacts with methanol solvent at room temperature to form an optically inactive solution. Identify the type of reaction for each case and illustrate the predicted optical activity measurements with annotated reaction mechanisms. 10 pts

3. Nicotine can be made when the following ammonium salt is treated with a weak base. Draw a stepwise mechanism for this reaction and write the structure of nicotine. 12 pts

\[
\text{Br} \quad \begin{align*}
\text{H} \quad \text{NaO} \quad \text{COONa} \\
\text{N} \quad \text{DMF} \quad 55 \, ^\circ \text{C} \\
\text{Br} \\
\text{O} \\
\text{O} \\
\text{N} \quad \text{H} \quad \text{Br} \quad \text{H} \\
\text{CH}_3 \quad \text{Br} \quad \text{Br} \\
\text{CH}_3 \quad \text{Br} \quad \text{Br}
\end{align*}
\]

nicotine (C\text{10}H\text{14}N\text{2}) + NaHCO\text{3} + NaBr
4a. When trichloride A is treated with one equivalent of methanol, nucleophilic substitution exclusively forms dihalide B. Draw a mechanism for this reaction. 8 pts

4b. Explain the high substitution reactivity of the red Cl group and make predictions about the type of substitution reactivity expected at the blue and black positions. Use annotated structures & orbitals to make your point. 8 pts

4c. It is proposed to make C from B using excess sodium acetate in 55 °C CH₃OH. Will this work? **YES/NO** (4 pts)

5. Which reagent in each pair would be the more reactive nucleophile in a polar protic solvent? Circle your answer. 2 pts each

   a. CH₃OH or (CH₃NH₂)
   b. CH₃O⁻ or H₂C- COO⁻
   c. Cl⁻ or F⁻
   d. H₂O or H₂O⁺
   e. HO⁻-SO⁻ or H₂C- COO⁻
   f. Me₃P or Me₃N

6. Predict the major product formed when each compound is treated with hot (55 °C) NaOCH₃/CH₃OH. 12 pts (3 pts each)
7. Starting with 1-methylcyclohexan-1-ol and using any other needed reagents, outline a synthesis of the following deuterium-labeled compound. You DO NOT need to show any mechanistic detail. 5 pts

8a. Recall that Hughes and Ingold devised a clever experiment that provided evidence for backside attack in the S_n2 reaction. What would their data have looked like if the reaction proceeded with exclusive frontside attack? 5 pts

8b. What would the filled/empty nucleophile-electrophile orbitals look like in a frontside transition-state? 5 pts

9. Propose the most efficient synthesis of 2-methoxy-3-methylbutane using starting materials containing 5 or fewer carbon atoms. You may use any other needed reagents and you DO NOT need to show any mechanistic detail. 5 pts

10. A recent paper in the Journal of the American Chemical Society reported the following data for 1,4,7-trimethylxatriguane 1:

One of these reactions is mechanistically surprising, from the standpoint of Table 6.6/6.7. Which is it, and what aspect of the data is causing you to classify it as ‘surprising.’ Explain your reasoning with an arrow-pushing mechanism using a truncated structure. Suggest an additional experiment to lend further support for the mechanistic nature of this surprising transformation. 5 pts

The elimination reaction is not surprising.

The substitution reaction appears to proceed via S_n2 - only one diastereomer found, surprising because of the tertiary nature:

could study reaction as

a function of [Br^-] and

see if rate law is

bimolecular.
## Chemistry 110a
THIRD EXAM
October 16, 2015

Name (print)__________________________________________

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All exam percentages were raised by 10%. 