Some Topics to Study (very broad):

**Reactivity stuff**
Classify atoms as electrophilic or nucleophilic
Definitions of nucleophiles/electrophiles
Nucleophiles
Leaving groups
Solvent types
pKa of common acids
Steric hindrance
Arrow-pushing

**S_N2**
Mechanism
Stereochemistry
Transition state
Reaction coordinate diagram
Inter and intramolecular examples
Solvent trends / solvation

**S_N1**
Mechanism / solvolysis
Stereochemistry
Transition state
Reaction coordinate diagram
Solvent trends

**E1 and E2**
Mechanisms
Stereochemistry
Solvent/reaction condition trends

**Alcohol Synthesis**
Nucleophilic additions to carbonyls
NaH vs. NaBH$_4$ / LiAlH$_4$
Organolithium reagents / Grignard reagents
Oxidation / chromium reagents
Retrosynthetic analysis

*PRACTICE QUESTIONS...*
1. Consider the following solvents. For each, draw the structure and circle the appropriate solvent classification.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>Classification: (Circle one answer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) isopropanol</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
<tr>
<td>b) DMF</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
<tr>
<td>c) HMPA</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
<tr>
<td>d) Acetone</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
<tr>
<td>e) THF</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
<tr>
<td>f) water</td>
<td><img src="image" alt="Structure" /></td>
<td>polar, protic&lt;br&gt;polar, aprotic&lt;br&gt;nonpolar, aprotic</td>
</tr>
</tbody>
</table>
2. For each compound shown below indicate whether the compound is nucleophilic or electrophilic at the marked atom (*).

a)  

b)  

c)  

d)  

e)  

3. Consider the following elimination reactions. For each:

a) draw the major product
b) determine if the elimination proceeds by E2 or E1 (circle your answer)

\[ \text{Br} \quad \text{NaOEt} \quad \text{EtOH} \quad \rightarrow \quad \text{E1 or E2} \]

\[ \text{OTs} \quad \text{MeOH, heat} \quad \rightarrow \quad \text{E1 or E2} \]

\[ \text{OH} \quad \text{cat. H}_2\text{SO}_4 \quad \text{benzene, heat} \quad \rightarrow \quad \text{E1 or E2} \]

\[ \text{Br} \quad \text{t-BuO}^+\text{K}^+ \quad \text{t-BuOH} \quad \rightarrow \quad \text{E1 or E2} \]
4. Consider the following substitution reactions. For each:
   a) draw the major product(s) that arise from substitution
   b) determine if the given substitution takes place by \( S_N2 \) or \( S_N1 \) (circle your answer)

   
   
   
   
   
   

5. 
   a) Which of the following two substrates would likely undergo faster E2 elimination (circle your answer)?

   
   
   or 

   
   

   b) Provide an explanation for your answer that includes 3-dimensional drawings.
6. Rank the following in order of nucleophilicity (1 being most nucleophilic, 4 being the least nucleophilic).

\[
\begin{array}{cccc}
\text{CH}_3\text{MgBr} & \text{EtOH} & \text{EtO}^- & \text{t-BuOH} \\
\end{array}
\]

7. Based on your knowledge of pKa values, rank the following in order of leaving group ability (1 being the best leaving group, 4 being the worst leaving group).

\[
\begin{array}{cccc}
\text{Br}^- & \text{TsO}^- & \text{CN} & \text{CH}_3 \\
\end{array}
\]

8. Draw a reaction coordinate diagram for the following reaction. Be sure to label starting material(s), transition state(s), product(s), activation energy(ies), and intermediate(s) (if applicable).

9. Provide reaction conditions for the following transformation (place your answers above and below the reaction arrows).
10. Provide a synthetic scheme for the following conversion.

11. Amanda has performed a retrosynthetic analysis on Compound F. After performing several disconnections, she arrived at bromobenzene and acetaldehyde (shown below). Provide a forward synthesis of Compound F that relies on Amanda’s strategy.
12. Grace has performed a retrosynthetic analysis on Compound A. After performing several disconnections, she arrived at allyl bromide and carbon dioxide (shown below). Provide a forward synthesis of Compound A that relies on Grace’s strategy.

![Diagram of retrosynthetic analysis](image)

13. Draw an arrow-pushing mechanism for the following transformation.

![Arrow-pushing mechanism image](image)

14. Draw an arrow-pushing mechanism for the following solvolysis experiment.

![Arrow-pushing mechanism image](image)

15. Draw an arrow-pushing mechanism for the following elimination reaction.

![Arrow-pushing mechanism image](image)
**Chem 14D Exam 1**

Spring 2010 / Prof. Neil Garg

Friday, April 23, 2010
1:00–1:50 PM

**General Instructions:**

This is a standard closed-note exam.

Please read each question carefully and write your answer neatly in the space provided using a black or blue pen (no pencils!).

You may use the back of the pages and page 6 as scrap paper.

The use of model sets is allowed.

A periodic table is provided on the last page of the exam.

Cell phones, calculators, headphones are not permitted.

*Keep your Student ID card out for ID Check.*

**GOOD LUCK!**