Statistics:
- **Average:** 74 pts (74%)
- **Highest:** 96 pts (96%); **Lowest:** 39 pts (39%)
- Number of students performing **at or above average:** 62 (57%)
- Number of students performing **below 55%:** 9 (8%)
- Number of students performing **at or above 90%:** 10 (9%)

1. (10 pts) Mark as true (T) or false (F) the following statements. Do not explain!
   - (F) A molecule with two chirality centers has two enantiomers;
   - (F) If two molecules are mirror images, they are always enantiomers;
   - (T) Some constitutional isomers are chiral;
   - (F) Every chiral compound has a diastereomer;
   - (F) Some achiral compounds are optically active;
   - (T) Diastereomers are not mirror images;
   - (F) $S_N2$ reactions require two molecules of substrate;
   - (T) Nucleophiles are Lewis bases;
   - (T) Hydrogenation of alkynes is a *syn*-addition process;
   - (T) Hydration of terminal alkynes obeys the Markovnikov rule;

2. Circle ALL that apply:
   A. (2 pts) Enantiomers:
      a. Have the same relative configuration;
      b. Have the same absolute configuration;
      c. **Rotate the plane of polarized light in opposite directions**;
      d. Are chiral molecules;
   B. (2 pts) $S_N1$ reactions:
      a. **Involve formation of carbocations**;
      b. Occur with retention of configuration;
      c. Occur fastest in polar protic solvents;
      d. Require strong nucleophiles;

3. (4 pts) Provide structures for the following compounds:
   - acetylene
   - (S)-3-chloro1-pentyne
   - (R)-3-butyln-2-ol
   - sodium amide

4. (2 pts) Which of the following statements is false:
   A. Achiral molecules are optically inactive
   B. **Meso compounds contain equal amounts of enantiomers**
   C. Racemic mixtures are optically inactive
   D. Enantiomers have specific rotations which are equal, but have opposite sign

5. (2 pts) Compound X, C$_3$H$_{10}$O, is **optically active**. The compound consumes one equivalent of hydrogen to give C$_3$H$_{12}$O. The hydrogenation product is also **optically active**. Based on this information, identify X among the structures below:
6. (3 pts) An isomer of hexene undergoes epoxidation to produce an achiral product. Select the correct starting material among the compounds below. Support your answer by a brief explanation.

![Chemical structures of hexenes and a chiral compound](image)

7. (3 pts) Assign absolute configurations to all chirality centers in cephalaxin (Keflex), the most widely prescribed antibiotic in the US.

![Structure of cephalaxin](image)

8. (6 pts) Identify the chiral molecules among the structures below:

![Chemical structures of various compounds](image)

9. (6 pts) Consider the following pairs of structures. Identify the relationship between the two components of each pair (same, constitutional isomers, enantiomers, diastereomers, not isomers).

![Pairs of structures](image)

10. (4 pts) Write an acceptable 3-dimensional structural presentation (i.e. a Fischer projection, bold-and-dashed wedge, etc., properly and unambiguously showing stereochemistry) for each of the following compounds.

A. (2S, 3R)-2,3-dichloropentane;

![Structure of (2S, 3R)-2,3-dichloropentane](image)

B. meso-1,3-dichlorocyclopentane;

![Structure of meso-1,3-dichlorocyclopentane](image)
11. (2 pts) Which of the following cannot act as a nucleophile? Explain!
   A. NH₃
   B. H₂O
   C. I⁻
   D. CH₃

   **Answer:** CH₃, because it doesn’t have any lone pairs of electrons, and therefore cannot serve as an electron donor (i.e. nucleophile).

12. (3 pts) Indicate the stronger nucleophile in each pair. Do not explain!

<table>
<thead>
<tr>
<th>methoxide anion or methanol</th>
<th>ammonia or PH₃</th>
<th>fluoride anion or iodide anion</th>
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</thead>
<tbody>
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</tr>
</tbody>
</table>

13. (2 pts) Consider the reaction of each of the following with 1-bromopentane. Which one would give the highest elimination/substitution ratio?
   A. NaOCH₂CH₃, ethanol, 55 °C
   B. NaSH, ethanol-water, 25 °C
   C. KOCH₃CH₃, (CH₃)₂COH, 55 °C
   D. KCN, DMSO, 40 °C

   **Answer:** The highest elimination/substitution ratio will be produced in the case (C). Both (A) and (C) involve the use of a strong nucleophile/base, but in (C) the species is bulkier, steering the process to elimination.


   1 - most reactive
   3
   2
   4

15. (10 pts) Write the product (or products) you would expect to obtain in each of the following reactions. In case of a mixture, indicate which product you expect to be the major component.

   

16. (4 pts) When alkynes react with halogen/water, the products are not halohydrins (as in the case of alkenes) but haloketones. Suggest a detailed mechanism for the following conversion:

   \( \text{C}_2\text{H}_5\text{CO}_2\text{H} \xrightarrow{\text{I}_2, \text{H}_2\text{O}} \text{C}_2\text{H}_5\text{CO}_2\text{I} \)
17. (3 pts) Pure (S)-2-butanol undergoes racemization (i.e. becomes a racemic mixture of R- and S-isomer) upon standing in dilute sulfuric acid. Provide a brief structural account.

18. (4 pts) Give one example of each of the following:
   A. Polar aprotic solvent (Structure and name).
   
   \[
   \text{dimethyl formamide} \quad \left(\text{HCON}_2\text{H} \right)
   \]

   B. Strong nucleophile, which is a strong base (Structure and name).
   
   \[
   \text{hydroxide anion} \quad \left(\text{O}^- \right)
   \]

   C. A tosylate ester (Only structure, no name!)
   
   \[
   \text{tosylate ester} \quad \left(\text{OSO}_2\text{N} \right)
   \]

19. (2 pts) Give one specific example of a concerted reaction.

   \[
   \text{alkene} \quad \xrightarrow{\text{NaCN, DMSO}} \quad \text{alkyne}
   \]

20. (3 pts) Suggest a plausible synthetic sequence for the following transformation (More than one step required!!).

   \[
   \text{(R)-2-pentanol} \quad \xrightarrow{\text{TsCl, pyr}} \quad \text{(S)-2-iodopentane}
   \]
21. (6 pts) Write complete chemical equations (and predict the products) for the following reactions:

A. 2-pentyne and H₂/Lindlar catalyst;

\[
\text{H}_2 [\text{Lindlar}] \quad \text{2-pentyne} \quad \text{propyne}
\]

B. 4-Chloro-1-butyne and H₂SO₄/HgSO₄;

\[
\text{H}_2\text{SO}_4/\text{HgSO}_4 \quad \text{4-Chloro-1-butyne} \quad \text{4-Chloro-1-iodobutane}
\]

C. 3-heptyne and Na/liq. NH₃;

\[
\text{Na/liq. NH}_3 \quad \text{3-heptyne} \quad \text{3-heptyne}
\]

22. (5 pts) Provide the reagents (in the boxes) necessary to conduct the following transformations:

\[
\text{H}_2\text{SO}_4/\text{HgSO}_4 \quad \text{1)NaNH}_2/\text{liq. NH}_3 \quad \text{2)} \quad \text{iodoacetane}
\]

\[
\text{Na/liq. NH}_3 \quad \text{2)H}_2 \quad \text{Lindlar Pd}
\]

23. (4 pts) Suggest a sequence of reactions necessary to achieve the following transformation:

\[
\text{acetylene} \quad ??? \quad \text{epoxide}
\]

\[
\text{H-C≡C-H} \quad 1) \text{NaNH}_2/\text{liq. NH}_3 \quad 2) \text{H}_2\text{Br} \quad 2) \text{I} \quad 1) \text{NaNH}_2/\text{liq. NH}_3 \quad 2) \text{I} \quad \text{H}_2 \quad \text{Lindlar Pd}
\]

\[
\text{H}_2\text{Cl}_2 \quad \text{MCPBA} \quad \text{epoxide}
\]
24. (3 pts) For the following species, complete the Lewis structure and provide two additional valid resonance forms. Use the curved arrow formalism to show the flow of electrons. Rank the resultant resonance structures.

![Resonance Structures](image)

25. (2 pts) BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!). (R)-2-Bromobutane undergoes racemization to give equal quantities of (+)- and (-)-2-bromobutane, when treated with NaBr in DMSO. Provide an explanation.

![Reaction Mechanism](image)

Here are two explanations, borrowed from actual student answers:

**Explanation 1:** When (R)-2-bromobutane is treated with NaBr in DMSO, an S_N2 reaction takes place in which the new Br replaces the old Br. *Since inversion must occur*, all initial products will be (S)-2-bromobutane. However, as more (S) isomers are produced, the NaBr will begin to convert (S) back into (R) while still converting (R) into (S). Eventually an equilibrium will be reached in which equal amounts of (R) and (S) isomers are present, aka a racemic mixture.

**Explanation 2:** Bromide can react with the compound, displacing the other bromine and inverting the chirality. The reaction goes in both directions, favoring neither, so equilibrium is reached when the mixture is racemic.