A student tried to synthesize cyclohexyl benzamide, but the reaction did not work very well and instead of pure product the student got a mixture of three compounds. Dr. Katsamanis suggested the following separation scheme, but he did not tell the student which compound would be in each of the five flasks.

1. Which flask contains the cyclohexylamine?
2. Which flask contains the benzoic acid?
3. Which flask contains the amide?

4. Which of the above compounds is the most acidic?
5. Which of the above compounds is the least acidic?
Predict the product of each of the following reactions. Use the answers shown above.

6. \[
\text{CH}_3\text{COCH}_3 + \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{NaOEt}} \]

7. \[
\text{C}_6\text{H}_5\text{COOEt} \xrightarrow{\text{NaOEt}} \]

8. \[
\text{C}_6\text{H}_5\text{COCH}_3 \xrightarrow{\text{NaOEt}} \]

Consider the following reaction.

\[
\text{HBr} \]

Here are some possible products.

9. What is the predicted product at low temperatures?

10. What is the predicted product at high temperatures?

11. Which structure is chiral?
The mechanism of the Heck reaction is shown below. Use the diagram to answer the next four questions.

Heck Reaction

12. Which of the lettered reaction steps is a β-hydride elimination reaction?
13. Which of the lettered reaction steps is an oxidative addition reaction?
14. What is the electron count for compound (1).
   A. 14   B. 15   C. 16   D. 17   E. 18
15. What is the electron count for compound (3).
   A. 14   B. 15   C. 16   D. 17   E. 18

16. Predict the product of the following reaction.

\[
\text{C}_{11}H_{16}O
\]
17. Predict the product of the following reaction.

\[
\text{CH}_3\text{CH}_2\text{N}_3 + \text{H}_2/\text{Pd} \rightarrow \\
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{NCH}_2\text{CH}_3
\]

A B C D E

18. Predict the major monobromination product of the following reaction.

\[
\text{C}_6\text{H}_{12} + \text{NBS} \rightarrow \\
\text{C}_6\text{H}_{10}\text{Br}_1 + \text{C}_6\text{H}_{11}\text{Br}_2 + \text{C}_6\text{H}_{11}\text{Br}_3 + \text{C}_6\text{H}_{11}\text{Br}_4
\]

A B C D E

19. Predict the product of the following reaction of phthalaldehyde with water.

\[
\text{Phthalaldehyde} + \text{H}_2\text{O} \rightarrow \\
\text{C}_6\text{H}_4\text{CO}_2\text{H} + \text{C}_6\text{H}_4\text{CO}_2\text{H}
\]

A B C D E
20. When benzene is protonated the resulting ion is the cyclohexadienyl cation. Which of the following MOs is the best representation of the HOMO of this cation?

\[
\text{benzene} \xrightarrow{\text{H}^+} \text{cyclohexadienyl cation}
\]

21. Predict the product of the following reaction sequence.

\[
\begin{align*}
\text{OTMS} & \xrightarrow{\text{heat}} \text{HF} \\
\text{acetone} & \rightarrow \\
\end{align*}
\]

22. Predict the product of the following Mannich reaction.

\[
\begin{align*}
\text{2} \text{PhCHO} & + \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{\text{NH}_4\text{OAc}} \\
\end{align*}
\]
23. Wender’s synthesis of the sesquiterpene **damsinic acid** included a reaction similar to this one. Predict the product.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\xrightarrow{\text{heat}}
\]

\[
\begin{array}{cccc}
\text{A} & \text{B} & \text{C} & \text{D} \\
\text{E} & \text{F} & \text{G} & \text{H} \\
\end{array}
\]

24. Five compounds containing 15 carbons atoms each are shown below. Four of them are sesquiterpenes and formed without methyl or other carbon shifts. One structure is not a terpene. Identify the one that is not a terpene.
The above structures represent the eight D-aldohexose structures. Use them to answer the next three questions. Write the appropriate letter A-H from the above selection in the labeled blank on your answer sheet for each question.

25. Identify the following D-aldohexose. (5 points)

26. Identify the following D-aldohexose. (5 points)

27. Suppose you had an unknown D-aldohexose and ran the following tests. (10 points)

   a. Nitric acid oxidation of the unknown gave an optically active aldaric acid.

   b. Ruff degradation of the unknown followed by nitric acid oxidation gave an optically active aldaric acid.

   c. Ruff degradation of the unknown followed by a Kiliani-Fisher elongation gave two D-aldohexoses. One was identical to the original unknown, the second was new. Nitric acid oxidation of this new D-aldohexose gave a optically inactive aldaric acid.

Identify the unknown D-aldohexose.
28. If an acid chloride is allowed to react with hydroxylamine it gives a hydroxamic acid. Hydroxamic acids can be acylated with acyl chloride. (10 points)

\[
\text{OCH}_2\text{Cl} \xrightarrow{\text{NH}_2\text{OH}} \text{OCH}_2\text{N(OH)} \quad \text{HOC\text{CH}_3}\xrightarrow{\text{OCH}_2\text{Cl}} \text{OCH}_2\text{N(OCH}_3\text{)}
\]

When O-acylated hydroxamic acids are treated with base they undergo a reaction called the Lossen rearrangement to give amines. Write a curved arrow mechanism for the Lossen reaction clearly showing all the bond making and bond breaking steps.

\[
\text{OCH}_2\text{N(OCH}_3\text{)} \xrightarrow{\text{\text{-OH}}} \text{H}_2\text{O} \xrightarrow{\text{\text{-OH}}} \text{NH}_2
\]

29. The terpene fenhol can be isolated from fennel plants. Its biosynthetic pathway passes through the \(\alpha\)-terpynyl cation. Use the curved arrow formalism to show the bond breaking and bond making steps in this biosynthetic pathway. (10 points)

\[
\text{\(\alpha\)-terpynyl cation} \rightarrow \text{OH}
\]

30. Give a good high yield synthesis of the following compound starting with benzene and any other necessary reagents of four carbons or less. (10 points)

\[
\text{H}_3\text{C} \quad \text{H}_2\text{C} \quad \text{H}_2\text{C}
\]
31. **Alternariol** is a toxic metabolite of *Alternaria* fungi. It is an important contaminant in cereals and fruits. Its biosynthetic pathway starts with the synthesis of the intermediate compound shown below and continues as shown. **Alternariol** is a tricyclic compound with three six membered rings and one methyl group.

![Pathway Diagram]


Draw the structure of **alternariol**, \( C_{14}H_{10}O_{5} \). (10 points)

32. The compound shown below is a sesquiterpene called **selina-3-7(11)-diene**, a component of amyris wood oil. Propose a synthesis of selina-3-7(11)-diene starting with compounds containing five or fewer carbon atoms. (10 points)

**Hint:** You might want to utilize an intramolecular Diels Alder reaction as part of your synthesis.

![Selina-3-7(11)-Diene Diagram]
Use the following roadmap to answer the next four questions

The sesquiterpene epi-ß-bulnesene, $C_{15}H_{24}$, has been synthesized by the Ovaska research group. Their synthesis is outlined in the roadmap shown above. (20 points)

33. Give the reagent or reagents needed for the preparation of Intermediate 1. More than one step may be required.

34. Give the reagent or reagents needed for the preparation of Intermediate 2. More than one step may be required.


36. Intermediate 4 reacts with the reagent shown to give epi-ß-bulnesene. Give the structure of epi-ß-bulnesene.