Chemistry 51
Exam 2, Summer 2005

This is a closed book exam. The exam lasts 90 minutes. All answers must appear on the answer sheet. Only the answer sheet will be collected. Put your name on the answer sheet now. When the exam is over you must hand your answer sheet in promptly or a penalty may be assessed.

Give the products or missing reactants of the following reactions. Include stereochemistry.

1. [Diagram: 1,4-dimethylcyclohexa-1,4-diene]
   - KMnO₄, cold, dilute → HIO₄ → NH₂OH
   - 1,4-dimethylcyclohexa-1,4-diene

2. [Diagram: 2-methylbutan-1-ol]
   - CH₂OH
   - Na₂Cr₂O₇, acid, heat → SOCl₂ → benzene → AlCl₃
   - 2-methylbutan-1-ol

3. [Diagram: Ether]
   - C(CH₃)₃
   - Br
   - NaOCH₃
   - Ether

4. [Diagram: 3-methylbut-1-ene]
   - NBS
   - 3-methylbut-1-ene
5. \[ \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{aq. HBr} \quad \text{Ph} \quad \text{Ph} \quad \text{OCH}_3 \]

A, hydrocarbon  B, bromoalkane

6. \[ \text{2-methylpent-1-ene} \quad \xrightarrow{1. \text{B}_2\text{H}_6} \quad \xrightarrow{2. \text{H}_2\text{O}_2, \text{aq. NaOH}} \quad \xrightarrow{1. \text{CH}_3\text{MgBr}} \quad \xrightarrow{2. \text{dil acid}} \]

7. \[ \text{(Z)-4-hydroxypent-3-en-2-one} \quad \xrightarrow{\text{dil. acid}} \]

8. \[ \text{Ph} \quad \xrightarrow{\text{H}^+\text{Br}^-} \quad \text{50 deg} \]

9. \[ \text{peroxides} \quad \xrightarrow{\text{HBr}} \]
Provide reasonable mechanism for the following reactions. Use the curved arrow notation consistently.

10.  
\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{OCH}_3 & \quad \text{CH}_3\text{OH}, \text{H}^+ \\
\text{Ph} & \quad \text{OCH}_3
\end{align*}
\]

11.  
\[
\begin{align*}
\text{Ph} & \quad \text{acid} \\
\text{Ph} & \quad \text{CH}_3
\end{align*}
\]

12. A student attempts to make the semicarbazone derivative of a ketone by reacting semicarbazide, which is available from Carl as the dihydrochloride \((\text{NH}_2\text{NH(CO)NH}_2 \cdot 2\text{HCl})\), with the ketone. There is no reaction.

Upon seeking advice from the lab instructor the student is told to add sodium acetate to the mixture. The reaction now takes place. Give a complete explanation of what happened.
Provide a synthesis of the following compounds using benzene, ethanol and/or any inorganic as the source of all carbons in the target molecules. You may use the requested products of earlier questions in subsequent questions even if you were not able to make the compound in the earlier questions. D is deuterium.

13. Ethanoic acid (acetic acid)

14. CH₃CD₂OH

15.

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H3C  D  D  D  D
       |   |
      H3C D  
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16. An unknown compound, X, has the formula C₆H₈O₂.

X is optically inactive.

X does not yield a yellow precipitate when treated with NaOI.

X yields a silver mirror when treated with Ag(NH₃)₂⁺.

X does not react with periodic acid.

X reacts with hydrogen on a 1:3 molar ratio to yield A, C₆H₁₄O₂.

A is oxidized and an acidic compound, B, C₆H₁₀O₄, is formed.

B is titrated and found to have an equivalent weight of about 73.

X is subjected to ozonolysis and yields ethanal and compound C, C₄H₄O₃.

C does not yield a yellow precipitate when treated with NaOI.

C reacts with periodic acid.

Propose structures for X, A, B, and C.
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