Questions (1-3)

A student in the lab had a mixture of three compounds, 4-methylbenzoic acid, 4-methylcyclohexylamine and 1,4-dimethylbenzene. In order to separate the three compounds the following extraction (separation) scheme was followed. At the end of the procedure the student had six separate flasks containing either an aqueous or an ether solution. Locate each compound by designating the flask expected to contain each compound. Some relevant pKa data is given.

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{NH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
pKa = & \quad 4.4 & \quad 11
\end{align*}
\]

1. Which flask contains the 4-methylcyclohexylamine? (3 points)
   a. 1         b. 2         c. 3      d. 4     e. 6
   [c. 3]

2. Which flask contains the 4-methylbenzoic acid? (4 points)
   a. 1         b. 2         c. 4      d. 5     e. 6
   [b. 2]

3. Which flask contains the 1,4-dimethylbenzene? (3 points)
   a. 1         b. 2         c. 3      d. 4     e. 5
   [a. 1]
4. Bromobenzene reacts with potassium amide to form aniline. Identify the most important intermediate.

\[
\begin{align*}
\text{Br} & \quad \text{H}_2\text{N} \\
\text{Br} & \quad \text{H}_2\text{N} \quad \text{Br} \\
\text{H}_2\text{N} & \quad \text{Br} \\
\text{H}_2\text{N} & \quad \text{Br}
\end{align*}
\]

A                              B                                   C                               D                            E

5. Here are three possible syntheses of phenylpropylether. Which ones would work?

\[
\begin{align*}
i \quad \text{phenol} & \quad \text{NaOH} & \quad \text{CH}_2\text{CH}_2\text{Br} & \quad \text{phenylpropylether} \\
\text{ii} & \quad \text{alkyl alcohol} & \quad \text{NaOH} & \quad \text{phenylpropylether} \\
\text{iii} & \quad \text{alkyl alcohol} & \quad \text{NaH} & \quad \text{phenylpropylether}
\end{align*}
\]

a. only     b. iii only    c. ii or iii      d. i or iii      e. i or ii or iii

6. When the compound shown below is heated it undergoes a rearrangement to form an isomer. Identify the product.

\[
\begin{align*}
\text{heat} & \quad \text{isomer} \\
\text{C}_8\text{H}_{12}\text{O} & \quad \text{C}_8\text{H}_{12}\text{O}
\end{align*}
\]

A                  B                    C D                      E
7. Organometallic reactions can be classified into fundamental reaction types. Classify the following reaction.

\[
\begin{align*}
(C_6H_5)_3P & \quad \longrightarrow \quad Pd \quad \longrightarrow \quad P(C_6H_5)_3 \\
+ \quad (C_6H_5)_3P & \quad \longrightarrow \quad Pd \quad \longrightarrow \quad P(C_6H_5)_3 \\
\end{align*}
\]

a. Ligand association 
b. Ligand insertion 
c. Ligand dissociation 
d. Reductive elimination 
e. Oxidative addition

8. What is the electron count for the following transition metal complex?

\[
\begin{align*}
(C_6H_5)_3P & \quad \longrightarrow \quad Rh \quad \longrightarrow \quad P(C_6H_5)_3 \\
\end{align*}
\]

a. 14  b. 15  c. 16  d. 17  e. 18

9. Predict the product of the following reaction sequence.

\[
\begin{align*}
O \quad \longrightarrow \quad Br \quad \longrightarrow \quad NaOEt \quad \longrightarrow \quad Br \quad \longrightarrow \quad NaOEt \quad \longrightarrow \quad Cl_2[(C_6H_5)_3P]_2Ru \quad \longrightarrow \quad H \quad \longrightarrow \quad C_6H_5 \\
\end{align*}
\]

A  B  C  D  E
10. Consider the relative basicity of these three amines. Which statement is true?

\[ \text{NH}_2 \quad \text{NH}_2 \quad \text{NO}_2 \]

- a. Cyclohexylamine is the strongest base and aniline is the weakest base
- b. Cyclohexylamine is the strongest base and 4-nitroaniline is the weakest base
- c. Aniline is the strongest base and cyclohexylamine is the weakest base
- d. Nitroaniline is the strongest base and cyclohexylamine is the weakest base
- e. Nitroaniline is the strongest base and aniline is the weakest base

11. Which of the following syntheses of benzylamine is the least likely to work?

A. \[ \text{Br} \overset{\text{NH}_3 \text{ (large excess)}}{\longrightarrow} \text{NH}_2 \]

B. \[ \text{Br} \overset{\text{NaN}_3}{\longrightarrow} \overset{1. \text{LiAlH}_4}{\longrightarrow} \overset{2. \text{H}_2\text{O}}{\longrightarrow} \text{NH}_2 \]

C. \[ \text{O} \overset{\text{Br}_2 \text{NaOH}}{\longrightarrow} \text{NH}_2 \]

D. \[ \text{O} \overset{1. \text{LiAlH}_4}{\longrightarrow} \overset{2. \text{H}_2\text{O}}{\longrightarrow} \text{NH}_2 \]

E. \[ \text{Br} \overset{\text{NaCN}}{\longrightarrow} \overset{1. \text{LiAlH}_4}{\longrightarrow} \overset{2. \text{H}_2\text{O}}{\longrightarrow} \text{NH}_2 \]

12. Predict the product of the following reaction sequence.

\[ \text{CH}_3 \overset{\text{Cl}_2 \text{AlCl}_3}{\longrightarrow} \overset{\text{HNO}_3 \text{ H}_2\text{SO}_4}{\longrightarrow} \overset{\text{H}_2 \text{Ni}}{\longrightarrow} \overset{1. \text{NaNO}_2, \text{H}_3\text{O}^+}{\longrightarrow} \overset{2. \text{BF}_4^- \text{ heat}}{\longrightarrow} \text{F} \]

\[ \text{Cl} \text{A} \quad \text{F} \text{B} \quad \text{Cl} \text{C} \quad \text{F} \text{D} \quad \text{Cl} \text{E} \]
13. Yifan (a visiting student from CHE 326) proposed the following synthesis for the April 13 Problem of the Day. Predict the product of his reaction sequence.

![Chemical structures and reactions](image)

The following short answer question should be answered in their designated spaces on your answer sheet.

14. Predict the main product of each of the following reactions. (10 pts)

a. ![Chemical structure and reaction](image)

b. ![Chemical structure and reaction](image)

15. Consider the following synthetic roadmap. In separate steps compounds X and Y are prepared. Then compounds X and Y are allowed to react in the presence of a palladium catalyst to give compound Z. Draw the structures of compounds X, Y and Z. (10 pts)
16. Use your knowledge of organometallic chemistry to propose a synthesis of the compound shown below. Your carbon starting materials may include 1,2-dibromobenzene and any other carbon containing compounds of four carbons or less. (10) points

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{trans double bond} & \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

17. Propose a good synthesis of the appetite suppressant Fenproporex. (10) pts

Your carbon starting materials may include benzene and any other carbon containing compounds of four carbons or less.

\[
\begin{align*}
\text{Br}_2 & \quad \text{FeBr}_3 \\
\text{Mg} & \quad \text{MgBr} \\
\text{O} & \quad \text{H}^+ \\
\text{PCC} & \\
\text{H}_2\text{N} & \quad \text{N} \\
\end{align*}
\]
**Challenge Question**

Under acid catalysis the amine shown below reacts with formaldehyde to give an intermediate compound. The intermediate compound fragments via subsequent steps to give two new compounds. Identify the two new compounds.

![Chemical Diagram](image)

*Hint: Consider a pericyclic reaction.*