CHM 2120 - Problem set 4

In this assignment:

- Oxidation of alcohols (review)
- Nucleophilic addition to carbonyls
- Esterification
- Saponification of esters
- 1. Provide names for the following compounds

- 2. Draw the structure corresponding to the following names:
 - a. (E)-2-butenal
 - b. 2-ethenylcyclohexanone
 - c. 4-oxohexanal
 - d. the benzyl carbocation
 - e. 1-phenylethanone (acetophenone)

3.

- a. Give the product of the following reactions
- b. Explain, using a mechanism, why the product from parts i and ii are different i.

OH
$$\frac{\text{Na}_2\text{CI}_2\text{O}_7}{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$$
ii.
OH $\frac{\text{PCC}}{\text{CH}_2\text{CI}_2}$
iii.

- 4. Can Grignard reactions be conducted in protic solvents? Explain.
- 5. How could you synthesize the following deuterium-labeled compound from benzene (note: D_2O is readily available)? (remember: $D = {}^2H$, an isotope of 1H)

6. Give the products of the following reactions:

a)
$$MgBr$$
 $1.$ H_3O^+

b)
$$\frac{\text{MgBr}}{2. \text{ H}_3\text{O}^+}$$

c) acetaldehyde
$$1.$$
 MgBr, Et₂O $2.$ H₃O⁺

d) acetone 1.
$$MgBr, Et_2O$$

e) Ph—=
$$C_2H_5MgBr$$

$$Et_2O$$

$$1. propanal, Et_2O$$

$$2. H_3O^+$$

f)
$$\frac{1. \text{ CH}_3\text{CH}_2\text{CH}_2\text{Li, Et}_2\text{O}}{2. \text{ NH}_4\text{Cl, H}_2\text{O}}$$

g)
$$\begin{array}{c}
 & 1. \text{ CH}_3\text{MgBr, Et}_2\text{O} \\
\hline
 & 2. \text{ H}_3\text{O}^+
\end{array}$$

h)
$$\underbrace{\frac{H}{1}}_{H} = 0 \quad \underbrace{\frac{1. \text{ NaBH}_{4}, \text{ MeOH}}{2. \text{ H}_{3}\text{O}^{+}}}_{}$$

7. Draw mechanisms for these reactions and show the stereochemistry of the product.

8. Suggest reagents to make the drug phenaglycodol by the route shown.

9. Suggest mechanisms for these reactions.

10. This reaction goes in one direction in acidic solution and in the other direction in basic solution. Draw mechanisms for the reactions and explain why the product depends on the conditions.

11. Why won't the following transformations work? Explain by showing the reaction that would happen instead.

a.

b.

c.

12. Provide a mechanism and the product for the following reactions:

a.

b.

c.

$$CO_2H$$
 H_2SO_4 OH

d.

e.

$$\begin{array}{c}
0 \\
0
\end{array}$$

$$\begin{array}{c}
1. \text{ NaOMe, MeOH} \\
2. \text{ H}_3\text{O}^+
\end{array}$$

f.

h.

i.

$$CO_2H$$
 H_2SO_4 $-H_2O$

j.

$$H_{CO_2H}$$
 H_2SO_4

k.

1.

$$\begin{array}{c|c} OH & O & O & H_2SO_4 \\ \hline CO_2H & \\ \hline salicylic acid & \\ \end{array}$$

13. Give a mechanism and product for each of the following reactions:

a.

b.

$$CI \xrightarrow{H_2N} OBn$$

c.

d.

OH
$$\frac{1. \operatorname{SOCl}_2}{2. \operatorname{OH}}$$
3. $\operatorname{H}_2\operatorname{N}$

14. Fill in the reagents required to accomplish the following transformations:

a.

$$OH$$
 OH

b.

c.

Suggest two other ways to synthesize the product shown in part c from starting materials containing only 4 carbons. The route can be completely different from the one used in part c.

d.