1. Halogenation Reactions I (*) 10 pts.

An unknown compound has the formula C₆H₁₄. It does not react with hydrogen. The compound is monochlorinated and the product is then fractionally distilled. Two fractions result. Both fractions are optically inactive. One contains only a single compound while the other consists of two compounds. Propose a structure for the original unknown (7 pts) and write down the approximate ratio for the two fractions obtained after chlorination (3 pts).

![Chemical structures and reactions]

2. Reactivity of alkenes, alcohols, ethers, epoxides, organometallic compounds and carbonyl groups (**) and (***) 25 pts.

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

2a. 4 pts

![Chemical reactions with stereochemistry notes]
2b. 4 pts

$$\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}$$

\[ \text{H}^+, \text{CH}_3\text{OH} \]

\[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \]

\((R)\)

2c. 6 pts

$$\begin{align*}
\text{KMnO}_4 & \\
\text{cold, dil alkaline}
\end{align*}$$

\[ \text{HIO}_4 \]

2d. 5 pts

$$\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \quad \text{OTs} \\
\text{CH}_3 & \quad \text{Ph}
\end{align*}$$

\[ \text{Acetic acid} \]

\[ \text{C}_{21}\text{H}_{18} \quad \text{C}_{23}\text{H}_{22}\text{O}_2 \]

2 products

Mechanism type A

OTs = tosylate

Rearrangement

Elimination

Substitution

(E1)

(SN1)
2e. 6 pts.

3. Halogenation reactions II (*) (5 pts): What type of reactive intermediate is formed in the reaction of propene with hydrogen bromide in the presence of peroxides to give 1-bromopropane?

a) 1° radical
b) 1° carbocation
c) 2° carbocation
d) 2° radical
4. Synthesis (**): (20 pts, 10 each). Propose a synthesis for the following products (on the right) by using the organic starting material(s) provided on the left and any other inorganic reagents, metals and solvents as needed:

4a. 10 pts

\[
\text{H-C≡C-H} \quad \text{and} \quad \text{Br} \quad \text{CH=CH}_2 \quad \text{Br} \quad \text{CH=CH}_2
\]

1. NaNH\(_2\) or NaH
2. H\(_2\)O
3. N\(_2\)O, H\(_2\)O

\[
\text{H-C≡C-H} \quad \text{CH=CH}_2 \quad \text{CH=CH}_2
\]

4b. 10 pts

\[
\text{H-C≡C-H} \quad \text{CH=CH}_2 \quad \text{OH}
\]

1. NaNH\(_2\)
2. CH\(_3\)CH\(_2\)Br
3. H\(_2\)O

\[
\text{H-C≡C-H} \quad \text{CH=CH}_2 \quad \text{CH=CH}_2 \quad \text{OH}
\]
5. Substitution Reactions (**) (5 pts).

For the SN2 substitution reactions below, predict which reaction would be faster (A or B) and explain your answer.

Internal SN2
Backside attack necessary for SN2
(Br and O anti)

A chair flip is necessary so that Br is anti to O
Less stable as ethyl group would be axial in this conformation

6. Hydrolysis (**). (5 pts) Which of the following compounds undergoes the most rapid hydrolysis reaction? Briefly explain the reason

a. 1
b. 2
Neighboring group effect of sulfur
(c. 3)
(d. 4)

Reason 2.5 pts

(internal SN2)

(salt)
(4)
(proton transfer
(salt)

6
7. Reactions of organometallic compounds and epoxides (*). (5 points) Which combination(s) of alkyl bromide and epoxide can be used to prepare the following product by addition of the Grignard reagent derived from the alkyl bromide to the epoxide.

![Chemical structures] (1) OH \(\rightarrow\) \(\text{EtBr}\) \(\text{EtBr}\)

1. only 1
2. only 2
3. only 1 and 3
4. only 2 and 4

8. Reaction mechanisms (** or ***). 20 pts. Propose a reasonable mechanism for these reactions.

7a. (10 pts)

\[ \text{H}_2\text{C} - \text{CH}_2 + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \]

acid ring opening

\[ \text{H}_2\text{C} - \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \]

back-side attack alcohol

proton transfer to solvent

\[ \text{H}_2\text{C} - \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \]
8.b. (10 pts)

PINACOL REARRANGEMENT

Untouched!

loss of H₂O

1,2 shift of methyl

more stable carbocation

→  + H₂O⁺
9. Epoxides (*). Which of the following general structures can be made by sequential reaction of epichlorohydrin with appropriate nucleophiles?

a. 1 
b. 2 
c. 3 
d. 4