Question 1

Which are the best reagents/conditions for the following reaction?

\[
\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}/\text{H}_2\text{SO}_4 \text{ (cat.)}} \text{CH}_3\text{CH} = \text{CHCH}_3
\]

A  H\text{}_2\text{O}/\text{H}_2\text{SO}_4 \text{ (cat.)}

B  1. BH\text{}_3\cdot\text{THF}
2. NaOH/\text{H}_2\text{O}_2

C  conc. H\text{}_2\text{SO}_4/\text{heat}

D  1. Hg(OAc)\text{}_2/\text{H}_2\text{O}
2. NaBH\text{}_4

Markovnikov-like addition of H\text{}_2\text{O} across the C=C bond WITH rearrangement, requires a carbocation intermediate and this a BRONSTED acid catalyst.
Question 2
MC26n
Which is MOST LIKELY to be the major product of the following reaction?

\[
\begin{align*}
\text{HBr} & \quad \text{CH}_3\text{OH} \\
\text{??？} & \\
\end{align*}
\]

\[\text{MeO}^+ : A \quad \text{B} : \text{OMe} \quad \text{C} \quad \text{D} \quad \text{OMe}^+ \]

\[\begin{align*}
\text{LB/BB} & \quad \text{BA/LA} \\
\text{MeO}^+ : \text{OMe} & \quad \text{OMe}^+ : \text{OMe} \\
\text{LB/BB} & \quad \text{BA/LA} \\
\end{align*}\]
**Question 3**

MCalkenesIh

Which is the expected major organic product of the following reaction

\[
\text{Br}_2 \quad \begin{array}{c} \text{EtOH (solvent)} \end{array} \]

- **A**
- **B**
- **C**
- **D**

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{OEt} \\
\text{Br}
\end{array}
\]

Br\textsubscript{2} is a Lewis acid that is strong enough to react with a C=C bond, EtOH is not, thus:

- The EtOH MUST add from the “top”.
- EtOH adds to the bromonium and not Br\textsuperscript{-} because there are many more EtOH molecules than Br\textsuperscript{-}.

Assume the Br\textsubscript{2} adds to the “bottom of the C=C bond” (if it added to the top a stereoisomer would result that is not important in the present context).
Question 4
MCalkenesIp

Which are the best reagents/conditions to perform the following reaction

A  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ (cat.)

B  1. BH$_3$.THF
   2. NaOH/$\text{H}_2\text{O}_2$

C  conc. $\text{H}_2\text{SO}_4$/heat

D  1. Hg(OAc)$_2$/H$_2$O
   2. NaBH$_4$

ANTI-Markovnikov addition of $\text{H}_2\text{O}$ across the C=C bond
WITHOUT rearrangement

Requires hydroboration
**Question 5**

MC26s

Which are the reagents and conditions that are most likely to give the products of the following reactions?

1) ![Diagram](image1)
   
   1. Hg(OAc)$_2$/H$_2$O
   2. NaBH$_4$

2) ![Diagram](image2)
   
   H$_2$O
   H$_2$SO$_4$ (cat.)/heat

3) ![Diagram](image3)
   
   1. BH$_3$/THF
   2. H$_2$O$_2$/$\sim$OH

A Reaction 1) H$_2$O/H$_2$SO$_4$ (cat.)/heat
   Reaction 2) 1. Hg(OAc)$_2$/H$_2$O, 2. NaBH$_4$
   Reaction 3) 1. BH$_3$/THF, 2. H$_2$O$_2$/$\sim$OH

B Reaction 1) 1. BH$_3$/THF, 2. H$_2$O$_2$/$\sim$OH
   Reaction 2) 1. Hg(OAc)$_2$/H$_2$O, 2. NaBH$_4$
   Reaction 3) H$_2$O/H$_2$SO$_4$ (cat.)/heat

C Reaction 1) 1. Hg(OAc)$_2$/H$_2$O, 2. NaBH$_4$
   Reaction 2) H$_2$O/H$_2$SO$_4$ (cat.)/heat
   Reaction 3) 1. BH$_3$/THF, 2. H$_2$O$_2$/$\sim$OH

D Reaction 1) 1. BH$_3$/THF, 2. H$_2$O$_2$/$\sim$OH
   Reaction 2) H$_2$O/H$_2$SO$_4$ (cat.)/heat
   Reaction 3) 1. Hg(OAc)$_2$/H$_2$O, 2. NaBH$_4$

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H$_2$O/H$_2$SO$_4$ (cat.)/heat results in Markovnikov-type addition of H$_2$O, but involves a carbocation intermediate that will rearrange if possible, as in these reactions.

1. Hg(OAc)$_2$/H$_2$O, 2. NaBH$_4$ results in Markovnikov addition of H$_2$O across the C=C bond, but avoids a carbocation intermediate, rearrangements do not occur, **this is the preferred method for Markovnikov water addition, do NOT use aqueous acid in a synthesis problem**.

1. BH$_3$/THF, 2. H$_2$O$_2$/$\sim$OH results in ANTI-Markovnikov addition of H$_2$O across the C=C bond, avoids a carbocation intermediate, rearrangements do not occur.
**Question 6**

MCalkenesIu

Give the best reagents/conditions to perform the following reaction:

![Chemical structure](image)

A. $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ (cat.)

B. 1. $\text{BH}_3$.THF  
    2. $\text{NaOH}/\text{H}_2\text{O}_2$

C. conc. $\text{H}_2\text{SO}_4$/heat

D. 1. $\text{Hg(OAc)}_2/\text{H}_2\text{O}$  
    2. $\text{NaBH}_4$

Markovnikov addition WITHOUT REARRANGEMENT must be oxymercuration.
Question 7
MC20q

Using the homolytic bond dissociation energies provided, which statement best describes the following reaction?

\[
\begin{align*}
\text{B. Reaction is exothermic by 5 kcal/mol} \\
\end{align*}
\]

A. The reaction is exothermic by 41 kcal/mol
B. The reaction is exothermic by 5 kcal/mol
C. The reaction is endothermic by 5 kcal/mol
D. The reaction is endothermic by 41 kcal/mol

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Even though the reaction involves heterolytic bond cleavage in Lewis acid/base reactions, we are only comparing the reactants and products.

The bond dissociation energies measure the energies of the electrons in bonds, and reactions involve breaking bonds and making new ones.

All we need to do is to compare the energy cost of breaking the bonds that are broken to the energy gain of the bonds that are made.

Energy "cost" due to breaking bonds = 86 (C-O) + 88 (H-Br)
Total = 174 kcal/mol

Energy "gain" due to making bonds = 68 (C-Br) + 111 (O-H)
Total = 179 kcal/mol

Electron energy in products lower than in reactants (the bonds are stronger in the products than in the reactants, thus the reaction is EXOTHERMIC by 179 - 174 = 5 kcal/mol
Only one of the following reactions actually gives the provide product, the other reactions actually give different products. Identify the correct reaction. (ignore stereochemistry in this problem)

A 4-ethyl-3-heptene \[ \xrightarrow{1. \text{BH}_3\cdot\text{THF}} \xrightarrow{2. \text{NaOH}/\text{H}_2\text{O}_2} \]

B 2-ethyl-2-heptene \[ \xrightarrow{1. \text{H}_2\text{O}/\text{Hg(OAc)}_2} \xrightarrow{2. \text{NaBH}_4} \]

C 3-ethyl-3-heptene \[ \xrightarrow{1. \text{BH}_3\cdot\text{THF}} \xrightarrow{2. \text{NaOH}/\text{H}_2\text{O}_2} \]

D 3-ethyl-3-heptene \[ \xrightarrow{1. \text{H}_2\text{O}/\text{Hg(OAc)}_2} \xrightarrow{2. \text{NaBH}_4} \]