Problem 1:

a) Draw the complete arrow-pushing mechanism for the reaction of 2-methyl-1,3-butadiene (isoprene) with 1 equivalent of HBr to produce 1-bromo-3-methylbut-2-ene. Make sure to include all lone pairs and non-zero formal charges.

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

\[ \overset{3^\circ}{\text{allylic C}^+} \]

\[ \overset{1^\circ}{\text{allylic C}^+} \]

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

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

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

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

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

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

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

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

2-methyl-1,3-butadiene

\[ \overset{\text{Br}^-}{\text{Br}^-} \]

1-bromo-3-methylbut-2-ene
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b) Is 1-bromo-3-methylbut-2-ene the kinetic or thermodynamic product? Explain.

This is the thermodynamic product as it has the more stable, more substituted alkene. The product that comes from the bromide attacking the $3^\circ$, allylic carbocation has a monosubstituted alkene and is thus the kinetic product.

c) Draw the structures of any other products that you expect to form in this reaction.
Problem 2:

a) Draw the structures of the products of this reaction in the boxes provided.

\[ \text{Br}_2 \text{ (1 equiv)} \rightarrow \]

\[ \text{kinetic product} \quad \text{thermodynamic product} \]

The reaction coordinate diagram for this reaction is show below:

Circle the correct terms:

b) At LOW/HIGH temperatures, the thermodynamic product is favored.

c) At LOW/HIGH temperatures, there is enough energy to overcome barrier \( E \) but not \( F \) or \( B \).

d) The formation of the thermodynamic and kinetic products is both ENDOTHERMIC/EXOTHERMIC

e) At LOW/HIGH temperatures, there is enough energy to overcome barriers \( E, F, \) and \( B \), but not \( A \).

f) The reaction to form the KINETIC/THERMODYNAMIC product proceeds at a higher rate at all temperatures.

g) The KINETIC/THERMODYNAMIC product is more stable because the alkene is more substituted.
**Problem 3:** Treatment of 1,3-butadiene with one equivalent of HBr leads to three products. One product is major, one is minor, and one is formed in only trace amounts (less than 1%). Which product is favored (kinetic or thermodynamic) depends on the reaction temperature.

a) Draw in the products of this reaction.

![Reaction products diagram](image)

b) The $^1$H NMR spectrum of one of the products is shown below.

![NMR spectrum](image)

Which product is this? Explain your answer.

The kinetic product has 3 vinyl protons while the thermodynamic and trace products have 2 vinyl protons. The $^1$H NMR data indicates 3 (or maybe 4?) vinyl protons. At this point we can be confident that this is the kinetic product because the other options have LESS than 3 vinyl protons.
Problem 4: Consider these molecular orbital diagrams. Notice that the relative energies of the MOs are shown, but the actual shapes of the MOs are omitted.

One of these diagrams is for the $\pi$ bond in an isolated alkene, and the other diagram is for a conjugated diene.

a) Fill in the electrons and label HOMO and LUMO on each diagram.

b) What effect does conjugation have on the relative energy of the HOMO?

Conjugation increases the energy of the HOMO

c) What effect does conjugation have on the HOMO-LUMO gap?

Conjugation decreases the magnitude of the HOMO-LUMO gap

d) In the Diels-Alder reaction, the dieneophile needs to be conjugated to an electron-withdrawing group for the reaction to proceed at a reasonable rate. Considering that the Diels-Alder reaction occurs via overlap of the filled HOMO on the diene with the empty LUMO on the dienophile, do you think the presence of the EWG raises or lowers the energy of the LUMO dienophile? Explain.

The presence of the EWG lowers the energy of the LUMO on the dienophile. This brings the LUMO closer to the energy of the HOMO of the diene. When these two orbitals are closer in energy, they overlap better and the reaction is more likely to occur.
Problem 5: Furan and thiophene are aromatic heterocycles that are similar in structure to the cyclopentadienyl anion.

a) Which of the following statements are true for all three compounds?
   i. They are aromatic
   ii. All of the atoms in the ring are sp² hybridized
   iii. They are 4π electron systems
   iv. They are weak bases

   A) I, II, and III   B) II and III   C) III and IV   D) II only   E) I, II and IV

b) Draw the conjugate acid of each compound in the boxes provided.

c) Which of the structures from part b) are aromatic? Explain.

Protonated furan and protonated thiophene are aromatic species. In both cases, the lone pair that was protonated was in the sp³ hybrid orbital (pointing out away from the aromatic ring), and the lone pair that remains is in the 2p orbital, still part of the aromatic system.

d) Which of the structures from part b) are nonaromatic? Explain.

The third molecule contains an sp³ hybridized carbon atom and is nonaromatic.

e) Are any of the structures from part b) antiaromatic? Explain.

No. To be antiaromatic requires a cyclic, planar structure with a 2p orbital on each atom in the ring and a total of 4n π electrons. None of these structures fit all of these criteria.