1. Label the allylic and vinylic hydrogens in the following molecules.

\[\text{a} = \text{allylic} \quad \text{v} = \text{vinylic}\]

(a) \(\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}\)

(b) \(\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{a} \quad \text{a} \quad \text{a}\)

(c) \(\text{CH}_3 \quad \text{a} \quad \text{a} \quad \text{CH}_3 \quad \text{a} \quad \text{v}\)

2. Write a second resonance structure for the following. Is the charge shared equally by both allylic carbons? If not, which one bears more charge?

(a) \[\begin{align*}
\text{CH}_2 &= \text{C} \\
\text{CH}_3 &= \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3
\end{align*}\]

The positive charge is on a 1° carbon in both resonance structures; therefore, both carbons share the positive charge equally.

(b) \[\begin{align*}
\text{CH}_3 &\quad \text{CH}_3 \\
2\text{o cation} &\quad 3\text{o cation}
\end{align*}\]

In this case, the 3° cation is more stable, therefore the charge is greater on that carbon, than the carbon of the 2° cation.

(c) \[\begin{align*}
3\text{o cation} &\quad 2\text{o cation}
\end{align*}\]

Same as in (b) – the charge resides on the 3° carbon more.
3. Draw resonance structures of the following.

(a) 
\[
\begin{array}{c}
\text{CH}_3\text{CH-CH=CH}_2 \\
\text{CH}_3\text{CH=CH-CH}_2
\end{array}
\]

(1 other structure)

(b) 
\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

(2 other structures)

(c) 
\[
\begin{array}{c}
\text{CH}_3\text{CH=CHC=CHCH}_2 \\
\text{CH}_3\text{CH=CHC=CHCH}_2 \\
\text{CH}_3\text{CH=CHC=CHCH}_2
\end{array}
\]

this is the least important resonance contributor

this is the most important resonance contributor

this structure is midway in importance

(d) 
\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

(1 other structure)

(e) 
\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

(3 other structures)

4. In Problem 3 a-d above, rate the different resonance structures in each group in order of relative quality. That is, which would be the most important contributor to the hybrid? The least? Justify your answer.

(a) 
\[
\begin{array}{c}
\text{CH}_3\text{CH-CH=CH}_2 \\
\text{CH}_3\text{CH=CH-CH}_2
\end{array}
\]

this structure is most stable

more stable = 2° allylic cation > 1° allylic cation = less stable
(b) 
\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\] 
\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]
these first two structures are equal in stability
\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]
this is the more important resonance contributor

more stable = $3^\circ$ allylic cation $> 2^\circ$ allylic cation $= \text{less stable}$

(c) 
\[
\begin{array}{c}
\text{CH}_3\text{CH}=\text{CH}-\overset{\bullet}{\text{C}}-\text{CH}=\text{CH}_2 \\
\text{CH}_3
\end{array}
\] 
\[
\begin{array}{c}
\text{CH}_3\text{CH}=\text{CH}-\overset{\bullet}{\text{C}}-\text{CH}=\text{CH}_2 \\
\text{CH}_3
\end{array}
\]
this is the least important resonance contributor
\[
\begin{array}{c}
\text{CH}_3\text{CH}=\text{CH}-\overset{\bullet}{\text{C}}-\text{CH}=\text{CH}_2 \\
\text{CH}_3
\end{array}
\]
this is the most important resonance contributor
\[
\begin{array}{c}
\text{CH}_3\text{CH}=\text{CH}-\overset{\bullet}{\text{C}}-\text{CH}=\text{CH}_2 \\
\text{CH}_3
\end{array}
\]
this structure is midway in importance

more stable = $3^\circ$ allylic radical $> 2^\circ$ allylic radical $> 1^\circ$ allylic radical $= \text{less stable}$

(d) 
\[
\begin{array}{c}
\text{CH}_2
\end{array}
\] 
\[
\begin{array}{c}
\text{CH}_2
\end{array}
\]
this is the more important resonance structure

more stable = $2^\circ$ allylic cation $> 1^\circ$ allylic cation $= \text{less stable}$
5. From the following compounds, choose the two that yield the same carbocation upon ionization.

These are the same carbocation because they are resonance structures of an allylic cation.

6. Show the products of the following reactions. Are the products in (a) and (b) the same molecule or different molecules? How about (c) and (d)?

(a) + 1 HCl (from 1,2-addition)

(b) + 1 HCl (from 1,4-addition)

The number designations show us these are the same molecule formed from 1,2- and 1,4-addition of HCl – 3-chlorocyclohexene.
These are different molecules formed from 1,2- and 1,4-addition of bromine.

7. Show the products of the following reactions. More than 1 product may be possible. To answer this properly, you will most likely need to consider the mechanism carefully (see the next problem).

(a) $\text{CH}_2\text{CH=CHCH}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{light}} \text{CH}_2\text{CH=CHCH=CHCH}_2\text{CH}_3$

(b) $\text{C}_8\text{H}_8\text{CH}_3 + \text{NBS} \rightarrow \text{C}_8\text{H}_8\text{CH}_2\text{Br} + \text{C}_8\text{H}_8\text{CH}_3$
8. Show the mechanism to justify your answers in Problem 7.

(a) \( \text{Cl}_2 \xrightarrow{\text{light}} \cdot \text{Cl} + \cdot \text{Cl} \)

\[
\begin{align*}
\text{CH}_2\text{CHCH} &= \text{CHCH}_2\text{CH}_3 + \cdot \text{Cl} \\
\delta^+ \cdot &\quad \delta^+
\end{align*}
\]

\[
\begin{align*}
\text{HCl} &\quad \text{HCl} + \text{Cl} - \text{Cl} \\
\uparrow &\quad \uparrow \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]

\[
\text{CH}_2\text{CHCH} &= \text{CHCH}_2\text{CH}_3 + \cdot \text{Cl} \\
\uparrow &\quad \uparrow
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CHCH} &= \text{CHCH}_2\text{CH}_3 + \cdot \text{Cl} \\
\text{HCl} &\quad \text{HCl} + \text{Cl} - \text{Cl} \\
\uparrow &\quad \uparrow \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CHCH} &= \text{CHCH}_2\text{CH}_3 + \cdot \text{Cl} \\
\text{HCl} &\quad \text{HCl} + \text{Cl} - \text{Cl} \\
\uparrow &\quad \uparrow \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]
(b) CH₂H

\[ \text{CH}_2\text{Br} \]

\[ \text{CH}_2\text{Br} \]

\[ \text{CH}_3\text{H} \]

\[ \text{CH}_3\text{H} \]

\[ \text{CH}_3\text{Br} \]

\[ \text{CH}_3\text{Br} \]

and

\[ \text{Br}_\text{CH}_2\text{CH}_2\text{Br} \]

\[ \text{Br}_\text{CH}_2\text{CH}_2\text{Br} \]

\[ \text{Br}_\text{CH}_2\text{CH}_2\text{Br} \]

\[ \text{Br}_\text{CH}_2\text{CH}_2\text{Br} \]

(same product)
and

\[
\text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br} + \text{CH}_3
\]

(c) 
\[
\text{Br} \quad \alpha \quad \beta \quad \Theta \text{OEt} \quad \text{EtOH} \quad \text{EtOH} \quad \text{EtOH}
\]

(d) 
\[
\text{CH}_3\text{CH}═\text{CH}═\text{CH}_2 \quad \text{H}_2\text{SO}_4 \quad \text{heat} \quad \text{CH}_3\text{CH}═\text{CH}═\text{CH}_2 \quad \Theta \text{OH}_2 \quad \Theta \text{OH}_2
\]
Note: In the first step, the bromonium ion is not formed. This is because the allylic cation is more stable, because of resonance properties.
Note: you would not normally expect to see a primary cation form (step 2). However, this is an allylic cation, and is resonance stabilized.

9. Show how to carry out the following syntheses, using any needed organic and inorganic reagents. Some may require several steps.

(a) \[ \text{NBS} \rightarrow \text{Br} \]

(b) \[ \text{Br}_2 \rightarrow \text{Br} \]
10. Show the two possible products of 1,2-addition of HCl to 2-methyl-1,3-butadiene. Their formation is temperature dependent. Which one would be favored at lower temperature and which one would be favored at higher temperature? Why?

Route 1 forms the less stable carbocation. Thus, it has the higher activation energy. It would not be favored at lower temperatures. However, it leads to the more stable product. This reaction path would be favored at higher temperatures.

Route 2 forms the more stable carbocation. It would have a lower activation energy, and would be favored at lower temperatures.
11. Explain the following in terms of kinetic and thermodynamic control. You will need to draw a potential energy diagram to fully complete your answer.

\[
\begin{align*}
\text{major} & \quad + \quad \text{minor} \\
\text{major} & \quad + \quad \text{minor}
\end{align*}
\]
1,2-addition is favored at lower temperatures, because $\delta^+$ is greatest on the 3° carbon in the allylic cation. Br$^-$ will attack here preferentially, because it has a lower $E_a$.

1,4-addition is favored at higher temperatures. The activation energy leading to the 1,4-adduct is higher, but $E_a$ is not as important as temperature rises. Instead, the equilibrium will favor the more stable product, which is the tetrasubstituted alkene.
12. Show the product and appropriate stereochemistry of the following Diels-Alder reactions.

(a) ![Diagram showing Diels-Alder reaction (a)]

(b) ![Diagram showing Diels-Alder reaction (b)]

(c) ![Diagram showing Diels-Alder reaction (c)]

(d) ![Diagram showing Diels-Alder reaction (d)]

13. Show the reagents (diene and dienophile) that would yield the following Diels-Alder adducts.
(a) \[ \text{Reaction} \Rightarrow \text{Product} \]

(b) \[ \text{Reaction} \Rightarrow \text{Product} \]

(c) \[ \text{Reaction} \Rightarrow \text{Product} \]