CHAPTER 10 HW SOLUTIONS: ALKENES

CIS-TRANS AND EZ ISOMERISM

1. Classify each structure as either cis, trans, E, or Z. Then beside each, draw the related stereoisomer (e.g. if the E isomer is shown, draw the Z isomer).

<table>
<thead>
<tr>
<th>Structure and Stereoisomer</th>
<th>cis, trans, E, or Z?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>trans or E</td>
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<tr>
<td></td>
<td>cis or Z</td>
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<tr>
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<td></td>
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<tr>
<td></td>
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2. Draw the following:

a. Z-2-bromo-4-methyl-2-pentene

b. Two stereoisomers of C₅H₁₀

(cloth diagram)

c. Two structural isomers of C₅H₁₀

(cloth diagram)
3. Give the IUPAC name for each compound, including cis/trans, R/S, or E/Z stereochemistry where necessary.

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<tr>
<td><img src="image1" alt="Structure" /></td>
<td>5-ethyl-2-methyl-2-octene or 5-ethyl-2-methyl-oct-2-ene</td>
<td><img src="image2" alt="Structure" /></td>
<td>2-isopropyl-4-methyl-1-hexene or 4-methyl-2-(1-methylethyl)-1-hexene</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>(S)-4-methylcycloheptene</td>
<td><img src="image4" alt="Structure" /></td>
<td>trans-4-hexen-2-ol or (E)-4-hexen-2-ol</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td>5-butyl-2-cyclopentenol</td>
<td><img src="image6" alt="Structure" /></td>
<td>(Z)-2,4-dichloro-3-heptene</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /></td>
<td>1,8,8-trimethylcyclooctene</td>
<td><img src="image8" alt="Structure" /></td>
<td>(Z)-5-(1-methylbutyl)-4-undecene</td>
</tr>
</tbody>
</table>

**ALKENE REACTION WITH HX**

4. Give the curved arrow mechanism for the following reactions. In your mechanisms, include all lone pairs and formal charge.

**a.**

![Mechanism](image9)

**b.**

![Mechanism](image10)
5. For the following reaction,

\[
\begin{align*}
\text{alkene} + \text{HI} & \rightarrow \text{products} \\
\end{align*}
\]

a. Draw the curved arrow mechanism that shows formation of both products.

b. Draw the energy diagram for each reaction (both pathways superimposed on one diagram, or side-by-side to relative scale).

c. Identify the major product and explain why it is favored over the other product.

2-iodopentane is the major product because it is formed through a lower energy carbocation (2° versus 1°). The pathway going through the lower energy carbocation has a smaller \( E_a \), so 2-iodopentane is formed faster.

6. Explain which is expected to be the major product in this reaction. Use an energy diagram with your explanation.

\[
\begin{align*}
\text{alkene} + \text{HCl} & \rightarrow \text{products} \\
\end{align*}
\]

The mechanism leading to the major product involves a lower energy 3° carbocation, and so that process has a smaller \( E_a \) and the product forms faster. The other product is formed through a higher energy 2° carbocation.
7. In this reaction, both $\Delta H^\circ$ and $\Delta S^\circ$ are negative. Explain.

\[
\begin{array}{c}
\text{HCl} \\
\hline
\text{Cl}
\end{array}
\]

$\Delta H^\circ$ is negative in this reaction (exothermic, or favorable) as most addition reactions are, because the reaction replaces a relatively weak $\pi$ bond with stronger $\sigma$ bonds.

$\Delta S^\circ$ is also negative in this reaction (unfavorable) because two reactants are converted into one product. The entropy decreases because there are fewer ways to arrange one compound than two (there are fewer degrees of “freedom.”)

8. Give the curved arrow mechanism for these reactions.

a. \[
\begin{array}{c}
\text{HCl} \\
\hline
\text{Cl}
\end{array}
\]

b. \[
\begin{array}{c}
\text{HI} \\
\hline
\text{(same as product)}
\end{array}
\]

9. Explain why the major product in this reaction is Q, not R.

In the mechanism of this reaction, a $2^\circ$ carbocation is first formed (Markovnikov addition). A hydride shift is then likely to occur because it creates a lower energy $3^\circ$ carbocation. The mechanism progresses through the lowest energy intermediates it has access to ($3^\circ$ carbocation), making product Q major, from the rearrangement.
10. Explain why two products are formed in this reaction.

\[
\text{[Diagram of the reaction with products and intermediate]}\]

In the mechanism of this reaction, a 3\(^{+}\) carbocation is formed (shown above). This intermediate is trigonal planar (flat). The iodide nucleophile can attack the cation with equal probability from the front or back sides, leading to the two products shown (a racemic mixture is formed).

**HYDRATION**

11. For the following reaction,

\[
\text{[Diagram of the reaction with products]}\]

a. Give the curved arrow mechanism for the reaction, showing formation of both products.

```
\text{[Mechanism diagram with curved arrows]}\]
```

b. Explain which is the major product, and use a complete energy diagram with your explanation.

The major product is 1-methylcyclohexanol because the pathway leading to this product goes through a lower energy 3\(^{+}\) carbocation, instead of a 2\(^{+}\) carbocation. 1-methylcyclohexanol is formed faster (lower \(E_a\)).
12. Using the mechanism from the previous problem, explain if acid is catalytic or not in the hydration reaction. [Note: “acid” considers all strong acid forms such as H$_2$SO$_4$ and H$_3$O$^+$.]

Yes “acid” is catalytic:

- Acid accelerates the reaction by lowering the activation barrier. This is accomplished by making the leaving group better (neutral H$_2$O).

- Acid is not consumed in the process because it is regenerated at the end of the reaction. For every “protonate” step that uses acid, there is a “deprotonate” step that creates it.

13. Give the curved arrow mechanism for each reaction.

a. 

\[ \text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O} \]

b. 

\[ \text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} \]

c. 

\[ \text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{O}} \]
SUMMARY OF ALKENE REACTIONS

14. Give the major organic product for the following reactions. If a racemic mixture is expected, draw both products. If a rearrangement is probable, give the product from the rearrangement.

a. $\text{Br}_2$ 
   \[ \text{Br} \quad \text{Br} \]
   \[ \text{racemic} \]

b. $\text{Cl}_2$ 
   \[ \text{Cl} \quad \text{Cl} \]
   \[ \text{racemic} \]

c. $\text{excess HI}$ 
   \[ \text{I} \quad \text{I} \]
   \[ \text{racemic} \]

d. $\text{H}_2\text{SO}_4$ 
   \[ \text{OH} \]

HALOGENATION

15. Give the curved arrow mechanism for each reaction. Include all lone pairs and formal charge.

a. $\text{Br}_2$ 
   \[ \text{Br} \quad \text{Br} \]
   (racemic)

b. $\text{Cl}_2$ 
   \[ \text{Cl} \quad \text{Cl} \]
   (racemic)
16. Explain why the “anti” addition product is formed in this reaction and not the “syn” product.

The mechanism goes through a cyclic bromonium ion. The bromide nucleophile then reacts through an S_N2-like mechanism, which inverts the reacting center. This causes the product to be anti, as the attacking Br becomes opposite the leaving group Br.

17. Explain why a rearrangement occurs in reaction (1), but not reaction (2).

The intermediates of the two reactions are shown above.

Reaction (1) goes through a high energy carbocation. There is a large driving force to stabilize a carbocation (by transfer of charge from a 2° to a 3°), since they are so high energy because of the lack of octet.

Reaction (2) goes through a bromonium ion, which is high energy but not quite as “bad” as a carbocation because all atoms have an octet. There is not as much need to lower the energy, so no rearrangements occur.

18. Molecules X and Y both have a formula of C_5H_{10}. Propose a structure of X and Y that is consistent with the observations noted upon addition with a solution of Br_2.

Or other alkene isomers

Or other ring isomers
19. Give the curved arrow mechanism for each reaction.

a. \[ \text{H}_2\text{C} = \text{C} \rightarrow \text{Cl}_2 \stackrel{\text{H}_2\text{O}}{\rightarrow} \text{Cl} \rightarrow \text{Cl} \text{OH} \rightarrow \text{racemic} \]

b. \[ \text{Br}_2 \stackrel{\text{CH}_3\text{OH}}{\rightarrow} \text{Br} \rightarrow \text{racemic} \]

20. Explain the following:

a. The nucleophile mostly attacks the bromonium ion at position X, not position Y.

\[ \text{Br}^- \rightarrow \text{Br}^- \rightarrow \text{Br} \rightarrow \text{δ}^+ \text{CH}_3 \]

This reaction has partial S_N1 character because the leaving group has partially left before the nucleophile approaches. This leaves a partial positive charge on positions X and Y, but there is a greater δ+ at position X because it is more substituted and can stabilize the charge better. The nucleophile is more likely to add to the side with the greater δ+ (the more hindered side).

b. Two products are formed in equal amounts in this reaction.

\[ \text{Cl}_2 \text{H}_2\text{O} \rightarrow \text{Br}_2 \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{Br} \rightarrow \text{Br} \rightarrow \text{OH} \rightarrow \text{OH} \]

The alkene is flat, so will form the bromonium ion on both faces with equal probability. Since there are two bromonium ions formed, two products are made after water attacks through an S_N2-like mechanism.
21. Which is the expected major product from this reaction? (All are racemic.)

\[ \text{reaction} \]
\[ \text{product A} \]
\[ \text{product B} \]
\[ \text{product C} \]
\[ \text{product D} \]

22. Give the major organic product of each reaction. Indicate if a racemic mixture is expected.

a. \[ \text{alkene} \xrightarrow{\text{Br}_2} \text{product} \]
   - \( (\text{rac.}) \)

b. \[ \text{alkene} \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \text{product} \]
   - \( (\text{rac.}) \)

c. \[ \text{alkene} \xrightarrow{\text{Br}_2, \text{CH}_3\text{OH}} \text{product} \]
   - \( (\text{rac.}) \)

d. \[ \text{alkene} \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \text{product} \]
   - \( (\text{rac.}) \)

23. Fill in the boxes with the correct reagent(s) for each reaction.

a. \[ \text{alkene} \xrightarrow{\text{HBr}} \text{product} \]
   - \( \text{Br} \)

b. \[ \text{alkene} \xrightarrow{\text{Cl}_2} \text{product} \]
   - \( \text{Cl} \)

c. \[ \text{alkene} \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \text{product} \]
   - \( \text{Br} \)

SUMMARY OF ALKENE REACTIONS
24. Explain the following features of the hydroboration reaction below.

![Reaction diagram]

a. Three moles of alkene react with each mole of BH₃.

One mole of BH₃ reacts with 3 moles of alkene, because each reaction involves addition of an H and boron species, which can occur three times (3 B-H bonds exist). The intermediate formed before the hydrogen peroxide step is to the right.

b. The reaction is “regioselective.” (Explain why it is regioselective.)

The reaction is “regioselective” because it forms one constitutional isomer preferentially (reacts in one “region” preferentially). Of the two groups that are added in the first step (H and BH₂), the boron group is larger, so adds preferentially to the less hindered side (sterically controlled). The position of the boron is eventually the position of the alcohol.

c. The reaction is “stereoselective.” (Explain why it is stereoselective.)

The reaction is stereoselective because there is a preference to form fewer stereoisomers than are possible based on the number of chiral centers (it selects for one or more stereoisomers). The stereochemistry originates in the hydroboration step: since the H and boron add at the same time, they must add to the same face of the alkene (syn addition). The orientation of the boron group is retained when it is replaced with an OH in the hydrogen peroxide step. Therefore, because the H and BH₂ add syn, this makes the OH and the methyl anti.

25. Give the major organic product for each reaction, paying attention to stereochemistry (syn/anti). Indicate if a racemic mixture is expected.

![Product images]

26. Fill in the boxes with the correct reagents for each reaction.

![Reagent images]
SUMMARY OF ALKENE REACTIONS

27. Give the major organic product(s) of each reaction. Pay attention to stereochemistry and indicate if a racemic mixture is formed. If a rearrangement is probable, give the product from the rearrangement.

a. \[ \text{OCH}_3 \rightarrow \text{Br}_2 \rightarrow \text{BrH}_2\text{C} \rightarrow \text{BrOCH}_3 \] (rac.)

b. \[ \text{HCl} \rightarrow \text{Cl} \]

c. \[ \text{a. BH}_3 \rightarrow \text{b. H}_2\text{O}_2, \text{OH}^- \rightarrow \text{OH} \]

d. \[ \text{H}_2\text{SO}_4 \rightarrow \text{OH} \] (rac.)

e. \[ \text{Cl}_2 \rightarrow \text{Cl} \rightarrow \text{OH} \] (rac.)

SYNTHESIS

28. Devise a synthesis that can transform each starting material into the product shown. Show all synthetic intermediates and reagents. More than one step is needed in each synthesis.

a. \[ \text{Br} \rightarrow \text{Br} \rightarrow \text{Br} \] (rac.)

b. \[ \text{Br} \rightarrow \text{NaOH} \rightarrow \text{Br}_2 \rightarrow \text{Br} \rightarrow \text{Br} \] (E2)

c. \[ \text{OH} \rightarrow \text{OCH}_3 \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{OH} \rightarrow \text{OCH}_3 \]
29. Draw a tree diagram to show the expected splitting for the indicated hydrogen atom in each molecule. Then describe the splitting pattern (e.g. doublet of doublets).

\[ J_{ab} = 2 \text{ Hz}; \quad J_{bc} = 7 \text{ Hz} \]

\[ J_{ab} = 16 \text{ Hz}; \quad J_{bc} = 8 \text{ Hz} \]

ALKENE NMR

30. How many signals should ideally be present in the \(^1\text{H} \) NMR spectrum of each compound (how many different hydrogen environments are present)? Use labels (a,b,c...) to show which hydrogen atoms should be grouped together.

- a) 4 signals
- b) 4 signals
- c) 7 signals

31. Assign the \(^1\text{H} \) NMR spectrum to hydrogen atoms in the structure. Pay attention to splitting + relative \( J \)'s.
32. Determine a structure that matches the molecular formula and $^1$H NMR spectrum for each problem. Then assign all peaks in the $^1$H NMR spectrum to hydrogen atoms in the structure.

**C$_{10}$H$_{10}$O**

- a, b, c, d
- 2H, d, 3H, m, 1H, 1H
- c/d can be switched

**C$_{7}$H$_{12}$O$_2$**

- a, b, c
- 1H, m, 1H, d, 1H, m
- $J = 10.2$ Hz
- $J < 2$ Hz are not included in the splitting

**C$_{4}$H$_{9}$N**

- a, b, c, d, e, f
- 1H, s, 2H, q, 3H, t
- 1H, dd, 1H, dd, 1H, dd