Chapter 8 Homework—Alkenes: Reactions and Synthesis

SHORT ANSWER

Section 8-1
To answer the question(s) below consider the following reaction:

When cyclohexene reacts with chlorine in carbon tetrachloride the \textit{trans}-dihalide is formed.

\[
\begin{array}{c}
\text{Cl}_2 \\
\text{CCl}_4 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

1. Refer to Section 8-1. Write the complete stepwise mechanism for this reaction. Be sure to show all intermediate structures and all electron flow using arrows.

ANS:

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

2. Refer to Section 8-1. Since the two chlorine atoms add to opposite faces of the cyclohexene double bond, we say that the reaction occurs with:

a. syn stereochemistry
b. cis stereochemistry
c. anti stereochemistry
d. retention of stereochemistry

ANS:
c

3. Refer to Section 8-1. The observed stereochemistry of addition of chlorine to cyclohexene is explained by the intermediacy of a:

a. cyclonium ion
b. carbocation
c. carbene
d. chloronium ion

ANS:
d
4. Refer to Section 8-1. Provide the IUPAC name for the product of the reaction of cyclohexene with chlorine.

ANS: 
*trans*-1,2-dichlorocyclohexane

5. Draw both chair conformations of *trans*-1,2-dichlorocyclohexane on the templates provided below. Circle the *least* stable conformation.

ANS:

Section 8-2
Consider the reaction sequence below to answer the following question(s):

\[ \text{Ph} = \text{CH} = \text{CH} \quad \xrightarrow{\text{Hg(OAc)}_2, \text{H}_2\text{O/THF}} \quad \text{PhOH} + \text{HgOAc} \quad \xrightarrow{\text{NaBH}_4} \quad \text{Ph} + \text{H}_\text{g} \]
6. Refer to Section 8-2. Write the complete reaction mechanism for the first step of this reaction sequence. Show all electron flow with arrows and show all intermediate structures.

ANS:

7. Refer to Section 8-2. The intermediate in the first step of this reaction sequence is called a:

a. carbocation
b. cyclonium ion
c. mercurinium ion
d. mercapto species.

ANS: c

8. Refer to Section 8-2. In the second step of this reaction sequence, the organomercury compound is treated with sodium borohydride, NaBH₄, to yield the alcohol product. This replacement of a carbon-mercury bond with a carbon-hydrogen bond is termed:

a. an oxidation
b. a reduction
c. a hydroxylation
d. a cycloaddition

ANS: b
Consider the reaction below to answer the following question(s).

Alkenes may be hydrated by the hydroboration/oxidation procedure shown.

9. Refer to Section 8-3. The intermediate formed in the first step of this reaction is:

   ![Intermediate A](image1)
   ![Intermediate B](image2)
   ![Intermediate C](image3)
   ![Intermediate D](image4)

ANS: b

10. Refer to Section 8-3. Hydroboration of alkenes is an example of:

   a. a rearrangement reaction.
   b. a substitution reaction.
   c. an elimination reaction.
   d. an addition reaction.

ANS: d

11. Refer to Section 8-3. Hydroboration/oxidation of alkenes occurs with:

   a. *anti* stereochemistry.
   b. *trans* stereochemistry.
   c. *syn* stereochemistry.
   d. unpredictable stereochemistry.

ANS: c
12. Refer to Section 8-3. The regiochemistry of hydroboration/oxidation of alkenes is:

a. Markovnikov.
b. non-Markovnikov
c. subject to solvent effects.
d. unrelated to alkene structure.

ANS: b

Section 8-4
Consider the reaction below to answer the following question(s).

When dichlorocarbene is generated in the presence of an alkene, a dichlorocyclopropane is formed.

\[
\begin{align*}
\text{H}_2\text{C} & \text{CH}_3 \\
\text{H} & \text{H} \\
\text{C} & \text{C} \\
& + \text{CHCl}_3 \xrightarrow{\text{KOH}} \\
\text{H}_2\text{C} & \text{Cl} \\
\text{H} & \text{Cl} \\
\text{Cl} & \text{Cl}
\end{align*}
\]

13. Refer to Section 8-4. Write the complete stepwise mechanism for the formation of dichlorocarbene, CCl₂. Show all intermediate structures and show all electron flow with arrows.

ANS:

\[
\begin{align*}
\text{Cl} & \text{Cl} \\
\text{H} & \text{H} \\
\text{Cl} & \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \text{Cl} + \text{K}^+ : \text{OH} \rightarrow \text{Cl} & \text{Cl} + \text{H}_2\text{O} & \rightarrow \text{Cl} & + \text{KCl}
\end{align*}
\]

14. Refer to Section 8-4. Draw the complete Lewis electron dot structure for dichlorocarbene, CCl₂.

ANS:

\[
\begin{align*}
\text{Cl} : \text{Cl} : \text{Cl} : \text{Cl} : \text{Cl}
\end{align*}
\]
15. Refer to Section 8-4. In the reaction of an alkene with dichlorocarbene, the dichlorocarbene is the:

a. electrophile.
b. Lewis base.
c. nucleophile.
d. both b and c.

ANS: a

16. Refer to Section 8-4. The reaction of an alkene with dichlorocarbene is:

a. regiospecific.
b. Markovnikov.
c. stereospecific.
d. non-Markovnikov.

ANS: c

Section 8-5
The sequence of (1) alkene hydroxylation followed by (2) diol cleavage is often an excellent alternative to direct alkene cleavage with ozone. For this sequence below, answer the following question(s).

17. Refer to Section 8-5. Draw the structure of A.

ANS:

18. Refer to Section 8-5. Give the formula for reagent B.

ANS: HIO$_4$
Section 8-6
Predict the products of each reaction below. Indicate regiochemistry and stereochemistry when relevant.

19. $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Pd}}$

ANS:

$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Pd}}$

20. $\text{H}_3\text{C}\text{C}=$\text{H}\text{C}=$\text{H}\text{C}=$\text{CH}_3 + \text{CHCl}_3 \xrightarrow{\text{KOH}}$

ANS:

$\text{H}_3\text{C}\text{C}=$\text{H}\text{C}=$\text{H}\text{C}=$\text{CH}_3 + \text{CHCl}_3 \xrightarrow{\text{KOH}}$

21. $\text{C}_6\text{H}_5\text{CH}=$\text{CH}_2 + \text{Cl}_2 \xrightarrow{\text{H}_2\text{O}}$

ANS:

$\text{C}_6\text{H}_5\text{CH}=$\text{CH}_2 + \text{Cl}_2 \xrightarrow{\text{H}_2\text{O}}$
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22. 

\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]

\[ \text{1. } \text{OsO}_4, \text{ pyridine} \]

\[ \text{2. } \text{NaHSO}_3, \text{ H}_2\text{O} \]

ANS:

\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]

\[ \text{1. } \text{OsO}_4, \text{ pyridine} \]

\[ \text{2. } \text{NaHSO}_3, \text{ H}_2\text{O} \]

\[ \text{HO} \quad \text{HO} \]

23.

\[ \text{HO} \quad \text{HO} \quad \text{H}_2\text{O} \]

ANS:

\[ \text{HO} \quad \text{HO} \quad \text{H}_2\text{O} \]

24.

\[ \text{CH}_3 \quad \text{C} = \text{C} \quad \text{CH}_3 \]

\[ \text{Cl}_2 \quad \text{CCl}_4 \]

ANS:

\[ \text{CH}_3 \quad \text{C} = \text{C} \quad \text{CH}_3 \]

\[ \text{Cl}_2 \quad \text{CCl}_4 \]

25.

\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]

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

\[ \text{CH}_3 \quad \text{Zn(Cu)}, \text{ ether} \]

ANS:

\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]

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

\[ \text{CH}_3 \quad \text{Zn(Cu)}, \text{ ether} \]
26. \[ \text{ANS:} \] 

27. \[ \text{ANS:} \] 

28. \[ \text{ANS:} \] 

29. \[ \text{ANS:} \]
Section 8-7
Choose the best reagent from the list below for carrying out each transformation. Place the letter of the reagent in the blank to the left of the reaction.

a. 1. O₃  
   2. Zn, H₂O⁺  

b. 1. BH₃, THF  
   2. H₂O₂, NaOH, H₂O  

c. CHCl₃, KOH  

d. H₂O, H₂SO₄, heat  

e. 1. OsO₄  
   2. NaHSO₃, H₂O  

f. KMnO₄, acid  

g. CH₂I₂, Zn(Cu)  

h. 1. Hg(OAc)₂, H₂O  
   2. NaBH₄  

30. ______  
ANS: b  

31. ______  
ANS: a  

32. ______  
ANS: g  

33. ______  
ANS: h
Section 8-8
For each reaction below suggest structures for alkenes that give the indicated reaction products. There may be more than one answer in some cases.

34. \[ \text{H}_2 \xrightarrow{\text{Pd}} \] 
ANS: 
\begin{align*}
\text{or} & \quad \text{or} \\
\text{or} & \\
\end{align*}

35. \[ 1. \text{BH}_3, \text{THF} \] 
\[ 2. \text{H}_2\text{O}_2, \text{NaOH}, \text{H}_2\text{O} \] 
ANS: 
\begin{align*}
\text{or} & \\
\end{align*}

36. \[ \text{HBr} \xrightarrow{\text{ether}} \] 
ANS: 
\begin{align*}
\text{or} & \\
\text{or} & \\
\end{align*}
Section 8-9
To answer the question(s) below consider the following information:

In an abandoned laboratory has been found a flammable liquid, A, in a bottle bearing only the label "Compound A: C\textsubscript{7}H\textsubscript{12}." Government agents have offered you a considerable sum to determine the structure of this compound. After verifying the molecular formula by elemental analysis, you find that Compound A reacts with 1 mol equiv of hydrogen; and, after treatment with acidic KMnO\textsubscript{4}, Compound A gives the dicarboxylic acid C (see below). Another bottle from the same laboratory is labeled "Compound B (isomer of A)." Compound B also reacts with 1 mol equiv of hydrogen, but yields cyclohexanone after treatment with acidic KMnO\textsubscript{4}.

38. Refer to Section 8-9. How many degrees of unsaturation does Compound A possess?

ANS:
A saturated seven carbon compound should have the formula C\textsubscript{7}H\textsubscript{16} so compound A has \((16 - 12) + 2 = 2\) degrees of unsaturation.

39. Refer to Section 8-9. Suggest structures for A and B.

ANS:

Compound A

Compound B
40. Refer to Section 8-9. What was the other product formed in the KMnO₄ oxidation of B?

ANS: CO₂

41. Lyapolate Sodium, whose structure is shown below, is used as an anticoagulant. Identify the monomer unit(s) in lyapolate sodium.

\[ \text{CH₂=CHCH₂CH₄}_n \]

\[ \text{SO₃Na} \quad \text{SO₃Na} \]

ANS: H₂C=CH–SO₃Na

42. Povidone is produced commercially as a series of products having mean molecular weights ranging from about 10,000 to 700,000. Complexed with iodine, povidone yields an iodophor, marketed under the tradename Betadine, which is used as a topical anti-infective.

\[ \text{CH=CHCH₂CH₄}_n \]

Identify the monomer unit(s) in povidone.

ANS:

\[ \text{CH=CH₂} \]