7

ALKENES AND ALKynes I:
PROPERTIES AND SYNTHESIS.
ELIMINATION REACTIONS
OF ALKYL HALIDES

SOLUTIONS TO PROBLEMS

7.1 (a) \( (E)-1\text{-Bromo-1-chloro-1-pentene or } (E)-1\text{-Bromo-1-chloropent-1-ene} \)
(b) \( (E)-2\text{-Bromo-1-chloro-1-iodo-1-butene or } (E)-2\text{-Bromo-1-chloro-1-iodobut-1-ene} \)
(c) \( (Z)-3,5\text{-Dimethyl-2-hexene or } (Z)-3,5\text{-Dimethylhex-2-ene} \)
(d) \( (Z)-1\text{-Chloro-1-iodo-2-methyl-1-butene or } (Z)-1\text{-Chloro-1-iodo-2-methylbut-1-ene} \)
(e) \( (Z,4\text{S})-3,4\text{-Dimethyl-2-hexene or } (Z,4\text{S})-3,4\text{-Dimethylhex-2-ene} \)
(f) \( (Z,3\text{S})-1\text{-Bromo-2-chloro-3-methyl-1-hexene or } (Z,3\text{S})-1\text{-Bromo-2-chloro-3-methylhex-1-ene} \)

7.2 Order of increasing stability

7.3 (a), (b) 
\[ \text{H}_2 \text{Pt pressure} \]
\[ \Delta H^\circ = -119 \text{ kJ mol}^{-1} \]

(c) Yes, because hydrogenation converts each alkene into the same product.

106
Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

(f) Order of stability: trans-2-pentene > cis-2-pentene > 1-pentene

7.4 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetrasubstituted. 2-Methyl-2-pentene has a trisubstituted double bond.

(b) trans-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.

(c) cis-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.

(d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of trans-2-hexene is disubstituted.

7.5 The location of IR absorptions between 600 cm\(^{-1}\) and 1000 cm\(^{-1}\) due to out-of-plane bending of alkene C—H bonds can be the basis of differentiation.

(a) 2-Methyl-2-pentene, \(~800\) cm\(^{-1}\)

(2,3-Dimethyl-2-butene, no alkene C—H bonds

(b) cis-3-Hexene, 650–750 cm\(^{-1}\)

trans-3-Hexene, \(~960\) cm\(^{-1}\)

(c) 1-Hexene, \(~900\) cm\(^{-1}\) and \(~1000\) cm\(^{-1}\)

cis-3-Hexene, 650–750 cm\(^{-1}\)

(d) trans-2-Hexene, \(~960\) cm\(^{-1}\)

2-Methyl-2-pentene, \(~800\) cm\(^{-1}\)

7.6 \[
\text{Br} \quad \overset{\text{NaOEt}}{\text{EtOH, 55°C}} \quad \overset{\text{most}}{\text{least}}
\]
7.7 (a) \[ \begin{align*} 
+ \text{Br} & \quad \text{OK} \quad \text{heat} \\
+ \text{OH} & \quad \text{OK} \quad \text{heat} \\
\text{Major product} & \quad \text{Minor product} \end{align*} \]

(trisubstituted, more stable) (monosubstituted, less stable)

(b) \[ \begin{align*} 
+ \text{Br} & \quad \text{OK} \quad \text{heat} \\
+ \text{OH} & \quad \text{OK} \quad \text{heat} \\
\text{Major product} & \quad \text{Minor product} \end{align*} \]

(tetrasubstituted, more stable) (dissubstituted, less stable)

7.8 t-ButOK in t-ButOH

7.9 An anti coplanar transition state allows the molecule to assume the more stable staggered conformation,

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

whereas a syn coplanar transition state requires the molecule to assume the less stable eclipsed conformation.

7.10 cis-1-Bromo-4-tert-butylcyclohexane can assume an anti coplanar transition state in which the bulky tert-butyl group is equatorial.

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

The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.
On the other hand, for \textit{trans}-1-bromo-4-\textit{tert}-butylcyclohexane to assume an anti coplanar transition state, the molecule must assume a conformation in which the large \textit{tert}-butyl group is axial:

\[
\text{Br} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{Br}
\]

Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

7.11 (a) Anti coplanar elimination can occur in two ways with the \textit{cis} isomer.

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{Br} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} \\
\text{B} & \quad \text{B}
\end{align*}
\]

\textit{cis}-1-Bromo-2-methylcyclohexane

(b) Anti coplanar elimination can occur in only one way with the \textit{trans} isomer.

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{Br} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} \\
\text{B} & \quad \text{B}
\end{align*}
\]

\textit{trans}-1-Bromo-2-methylcyclohexane

7.12 (a) (1) \[
\text{CH}_3 + \text{H} \quad \text{CH}_3 + \text{H}
\]

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

(2) \[
\text{CH}_3 + \text{H} \quad \text{CH}_3 + \text{H}
\]

(3) \[
\text{CH}_3 + \text{H} \quad \text{CH}_3 + \text{H}
\]
(b) By donating a proton to the \(-\text{OH}\) group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group \((\text{H}_2\text{O})\) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic \(\text{OH}^-\) ion, and such steps almost never occur.

Order of increasing ease of dehydration

Steps (2) and (3), ionization and rearrangement, may occur simultaneously.

2-Methyl-2-butene
**ALKENES AND ALKynes I: PROPERTIES AND SYNTHESIS**

### 7.15 CH$_3$CH$_2$CH$_2$OH + H$_2$O $\xrightarrow{\text{H}^+ / \text{H}_2\text{O}}$ H$^+$CH$_2$CH$_2$CH$_2$OH$^-$ (H$_2$O) $\rightarrow$ HCH$_2$CH$_2$CH$_2$O$^-$ (H$_2$O)

2-Methyl-1-butanol

\[
\text{CH}_3\text{CH}(_2)^+\text{CH}_2\text{CH}_3 \xrightarrow{1,2\text{-hydride shift}^*} \text{CH}_3\text{CH}(_2)^+\text{CH}(_2)\text{CH}_3 + \text{H}_3\text{O}^+ \\
\]

\[
\text{CH}_3\text{C}(_2)\text{CH}_3 + \text{H}_3\text{O}^+ \\
\]

*The hydride shift may occur simultaneously with the preceding step.*

### 7.16 HO

Isoborneol

\[
\text{HO} \xrightarrow{\text{H}_2\text{O}^+ (\text{H}_2\text{O})} \text{CH}_3\text{CH}(_2)\text{CH}_3 \\
\]

Camphene

\[
\text{CH}_3\text{CH}(_2)\text{CH}_3 \xrightarrow{\text{H}_2\text{O}^+ (\text{H}_2\text{O})} \text{CH}_3\text{CH}(_2)\text{CH}_3 + \text{H}_3\text{O}^+ \\
\]

*The hydride shift may occur simultaneously with the preceding step.*
112 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

7.17 (a) \( \text{CH}_3\text{CH} \rightleftharpoons \text{CH}_2 + \text{NaNH}_2 \rightarrow \) No reaction

(b) \( \text{CH}_3\text{C} \rightleftharpoons \text{C} \rightleftharpoons \text{H} + \text{Na}^+ : \text{NH}_2 \rightarrow \text{CH}_3\text{C} \rightleftharpoons \text{C} \rightleftharpoons \text{Na}^+ + : \text{NH}_3 \)

\[ \text{Stronger} \quad \text{Stronger} \quad \text{Weaker} \quad \text{Weaker} \]

\[ \text{acid} \quad \text{base} \quad \text{base} \quad \text{acid} \]

(c) \( \text{CH}_3\text{CH}_2\text{CH}_3 + \text{NaNH}_2 \rightarrow \) No reaction

(d) \( \text{CH}_3\text{C} \rightleftharpoons \text{C} \rightleftharpoons \text{H} + \text{NH}_2 \rightarrow \text{CH}_3\text{C} \rightleftharpoons \text{CH} + :: \text{NH}_3 \)

\[ \text{Stronger} \quad \text{Stronger} \quad \text{Weaker} \quad \text{Weaker} \]

\[ \text{base} \quad \text{acid} \quad \text{base} \quad \text{acid} \]

(e) \( \text{CH}_3\text{C} \rightleftharpoons \text{C} \rightleftharpoons \text{H} + \text{NH}_3 \rightarrow \text{CH}_3\text{C} \rightleftharpoons \text{CH} + :: \text{NH}_3 \)

\[ \text{Stronger} \quad \text{Stronger} \quad \text{Weaker} \quad \text{Weaker} \]

\[ \text{base} \quad \text{acid} \quad \text{base} \quad \text{acid} \]

7.18

7.19 (a) \( \text{CH}_3\text{C} \rightleftharpoons \text{H} \rightarrow \text{Cl} \rightarrow \text{Cl} \rightarrow \text{PCl}_3 \quad \text{0}^\circ \text{C} \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{Cl} \quad \text{mineral oil, heat} \) \( \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{CH} \)

(b) \( \text{CH}_3\text{C} \rightleftharpoons \text{Cl} \rightarrow \text{PCl}_3 \quad \text{0}^\circ \text{C} \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{Cl} \rightarrow \text{mineral oil, heat} \rightarrow \text{CH}_3\text{C} \rightleftharpoons \text{CH} \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \) \( \text{mineral oil, heat} \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{CH} \)

(d) \( \text{CH}_3\text{C} \rightleftharpoons \text{Cl} \rightarrow \text{Br}_2 \rightarrow \text{CCl}_4 \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{Cl} \rightarrow \) \( \text{Br}_2 \rightarrow \text{CCl}_4 \rightarrow \) \( \text{CH}_3\text{C} \rightleftharpoons \text{CH} \)

7.20

(Starting the synthesis with 1-propyne and attempting to alkylate with a tert-butyl substrate would not work because elimination would occur instead of substitution.)
ALKENES AND ALKynes I: Properties and synthesis (113)

7.21

![Diagram of Compound A]

7.22

2-Nonyne

(1) Li, C₂H₂NH₂, −78°C

(2) NH₄Cl

(E)-2-Nonene

7.23

Route 1

\[
\begin{align*}
\text{HC} & \text{CCH₃CHCH₃} \\
& \text{NaNH₂ (−NH₃)} \\
& \text{Na⁺} \text{C} \text{CCH₃CHCH₃} \\
& \text{H₂, Pd, or Ni pressure} \\
& \text{CH₃CH₂CH₂CH₂CH₃}
\end{align*}
\]

Route 2

\[
\begin{align*}
\text{HC} & \text{C} \text{CH₃CHCH₃} \\
& \text{NaNH₂ (−NH₃)} \\
& \text{H₂, Pd, or Ni pressure} \\
& \text{CH₃CH₂CH₂CH₂CH₃}
\end{align*}
\]

Route 3

\[
\begin{align*}
\text{HC} & \text{CCH₃CHCH₃} \\
& \text{NaNH₂ (−NH₃)} \\
& \text{H₂, Pd, or Ni pressure} \\
& \text{CH₃CH₂CH₂CH₂CH₃}
\end{align*}
\]
**ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS**

### 7.24

(a) Undecane

\[ \text{HC} \equiv \text{C} \quad \text{CH}_3 \text{C} \equiv \text{C} \quad \text{CH}_2 \text{CH}_3 \text{C} \equiv \text{C} \quad \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{C} \equiv \text{C} \quad \text{C} \]

Etc. (using the other alkyne and alkyl halide homologue pairs)

2-Methylheptadecane

\[ \text{X(CH}_2\text{)}_3 \text{CH}_3 \quad \text{X(CH}_2\text{)}_3 \text{CH}_3 \quad \text{X(CH}_2\text{)}_3 \text{CH}_3 \quad \text{X(CH}_2\text{)}_3 \text{CH}_3 \]

(Note that \( \text{X} \text{C} \equiv \text{C}^{-} \text{X} \) is not a good choice because the alkyl halide is branched at the carbon adjacent to the one which bears the halogen.

Neither would \( \text{X} \text{C} \equiv \text{C}^{-} \text{X} \) work because the alkyl halide is secondary. Both of these routes would lead to elimination instead of substitution.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be

\[ \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \quad \text{R} \equiv \text{C} \equiv \text{C}^{-} \text{X} \quad \text{R} \equiv \text{C} \equiv \text{C}^{-} \text{R}' \]

\[ \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \quad \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \quad \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \]

\[ \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \quad \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \quad \text{RC} \equiv \text{C} \equiv \text{H} \quad \text{NaNH}_2 \]

### 7.25

(a) We designate the position of the double bond by using the lower number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is trans-2-pentene.
(b) We must choose the longest chain for the base name. The correct name is 2-methyl-propene.

![2-methyl-propene](image)

(c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.

![1-methylcyclohexene](image)

(d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.

![3-methylcyclobutene](image)

(e) We number in the way that gives the double bond and the substituent the lower number. The correct name is (Z)-2-chloro-2-butene or (Z)-2-chlorobut-2-ene.

![Z-2-chloro-2-butene](image)

(f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.

![3,4-dichlorocyclohexene](image)

7.26 (a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k) (l)
7.27  (a)  

\[ \begin{align*}  
& \text{(2Z,4R)-4-Bromo-2-hexene} \quad \text{or} \quad \text{(2Z,4R)-4-Bromohex-2-ene} \\
& \text{(2E,4R)-4-Bromo-2-hexene} \quad \text{or} \quad \text{(2E,4R)-4-Bromohex-2-ene} \\
\end{align*} \]

(b)  

\[ \begin{align*}  
& \text{(3R,4Z)-3-Chloro-1,4-hexadiene} \quad \text{or} \quad \text{(3S,4Z)-3-Chlorohexa-1,4-diene} \\
& \text{(3R,4E)-3-Chloro-1,4-hexadiene} \quad \text{or} \quad \text{(3S,4E)-3-Chlorohexa-1,4-diene} \\
\end{align*} \]

(c)  

\[ \begin{align*}  
& \text{(2E,4R)-2,4-Dichloro-2-pentene} \quad \text{or} \quad \text{(2Z,4R)-2,4-Dichloropent-2-ene} \\
& \text{(2E,4S)-2,4-Dichloro-2-pentene} \quad \text{or} \quad \text{(2Z,4S)-2,4-Dichloropent-2-ene} \\
\end{align*} \]
7.28 (a) \((E)\)-3,5-Dimethyl-2-hexene or \((E)\)-3,5-dimethylhex-2-ene
(b) 4-Chloro-3-methylcyclopentene
(c) 6-Methyl-3-heptene or 6-methylhept-3-ene
(d) 1-sec-Butyl-2-methylcyclohexene or 1-methyl-2-(1-methylpropyl)cyclohexene
(e) \((4Z,3R)\)-3-Chloro-4-hepten-1-yne or \((4Z,3R)\)-3-chlorohept-4-en-1-yne
(f) 2-Pentyl-1-heptene or 2-pentylhept-1-ene

7.29 1-Pentanol > 1-pentyne > 1-pentene > pentane
(See Section 3.8 for the explanation.)
118 ALKENES AND ALKynes I: Properties and Synthesis

7.30 (a) \[
\begin{align*}
\text{Cl} & \xrightarrow{\text{OK}} \text{Cl} \\
\text{ONa} & \xrightarrow{\text{OH}} \text{Cl}
\end{align*}
\]
(b) \[
\begin{align*}
\text{Cl} & \xrightarrow{\text{ONa}} \text{Cl} \\
\text{OH} & \xrightarrow{\text{OH}} \text{Cl}
\end{align*}
\]
(c) \[
\begin{align*}
\text{OH} & \xrightarrow{\text{HA, heat}} \text{Cl} \\
\text{OH} & \xrightarrow{\text{HA, heat}} \text{Cl}
\end{align*}
\]
(d) \[
\begin{align*}
\text{Br} & \xrightarrow{\text{H}_2\text{O}} \text{Cl} \\
\text{Cl} & \xrightarrow{\text{H}_2\text{O}} \text{Cl}
\end{align*}
\]
(e) \[
\begin{align*}
\text{Br} & \xrightarrow{\text{NaNH}_2(2\text{ equiv.})} \text{H}_2\text{Cl} \xrightarrow{\text{Ni}_2\text{B}(P-2)} \text{Cl}
\end{align*}
\]
(f) \[
\begin{align*}
\text{Br} & \xrightarrow{\text{H}_2\text{O}} \text{Cl} \\
\text{Cl} & \xrightarrow{\text{H}_2\text{O}} \text{Cl}
\end{align*}
\]

7.31 (a) \[
\begin{align*}
\text{Br} & \xrightarrow{\text{ONa}} \text{Cl} \\
\text{OH} & \xrightarrow{\text{OH}} \text{Cl}
\end{align*}
\]
(b) \[
\begin{align*}
\text{Cl} & \xrightarrow{\text{ONa(2 equiv.)}} \text{Cl} \\
\text{OH} & \xrightarrow{\text{OH}} \text{Cl}
\end{align*}
\]
(c) \[
\begin{align*}
\text{OH} & \xrightarrow{\text{HA, heat}} \text{Cl}
\end{align*}
\]

7.32 (a) \[
\begin{align*}
\text{NaNH}_2 & \xrightarrow{\text{aq\ NH}_3} \text{Cl} \\
\text{Na}^+ & \xrightarrow{\text{t-NaI}} \text{Cl}
\end{align*}
\]
7.33 We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use D₂ and a metal catalyst (Section 7.14).
7.34 (a) Br\(_2\) + 3NaNH\(_2\) → Na\(^+\) + NH\(_4\)Cl

7.34 (b) Br\(_2\) + 3NaNH\(_2\) → Na\(^+\) + NH\(_4\)Cl

7.35 Dehydrohalogenation and Dehydration

\[
\text{EtO}^+\text{CH}_3\text{H}^+\text{CH}_3\text{Br} \rightarrow \left[\text{EtO}^+\text{CH}_3\text{H}^+\text{CH}_3\text{Br}^-\right]_2 \rightarrow \text{H}^\text{CH}==\text{CCH}_3\]
7.36 Dehydration of trans-2-methylcyclohexanol proceeds through the formation of a carbo-
cation (through an E1 reaction of the protonated alcohol) and leads preferentially to the
more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene
(the minor product of the dehydration) because its double bond is more highly substituted.

\[
\begin{align*}
\text{CH}_3 \text{OH} & \quad \xrightarrow{\text{HA} - \text{H}_2\text{O}} \quad \text{CH}_3 \quad \xrightarrow{\text{HA} - \text{HA}} \quad \text{CH}_3 \\
& \quad \text{(major)} \quad \text{Trisubstituted double bond} \\
& + \quad \text{(minor)} \quad \text{Disubstituted double bond}
\end{align*}
\]

Dehydrohalogenation of trans-1-bromo-2-methylcyclohexane is an E2 reaction and must
proceed through an anti coplanar transition state. Such a transition state is possible only
for the elimination leading to 3-methylcyclohexene (cf. Review Problem 7.11).

\[
\begin{align*}
\text{Br} & \quad \text{H} \\
\quad & \quad \text{H} \\
\quad & \quad \text{H} \\
\quad & \quad \text{CH}_3 \\
& \quad \text{3-Methylcyclohexene}
\end{align*}
\]

7.37 (a) major + minor
(b) only product
(c) major (+ stereoisomer)

7.38 (a) major + minor
(b) only product
(c) major (+ stereoisomer)
122 ALKENES AND ALKynes I: PROPERTIES AND SYNTHESIS

(c) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] + \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

7.39 (a) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

(b) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

(c) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

(d) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

(e) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{Br} \]

7.40 \[
\begin{array}{c}
\text{CH}_3
\end{array}
\] \[ \text{CH}_2\text{CH}_2\text{CH}_3 \] \[ \text{CH}_3
\] \[ \text{OH} \] \[ \text{3°} \] \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \] \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \] \[ \text{2°} \]

7.41 (a) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{HA} \] \[ \text{heat} \] \[ (-\text{H}_2\text{O}) \]

(b) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{HA} \] \[ \text{heat} \] \[ (-\text{H}_2\text{O}) \]

(c) \[
\begin{array}{c}
\text{major} \\
\text{minor}
\end{array}
\] \[ \text{HA} \] \[ \text{heat} \] \[ (-\text{H}_2\text{O}) \] \[ (+ \text{ stereoisomer}) \]
**ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS**

7.42 The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

7.43 Only the deuterium atom can assume the anti coplanar orientation necessary for an E2 reaction to occur.

7.44 (a) A hydride shift occurs.
(b) A methanide shift occurs.

---

**Diagram:**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d)</td>
<td>$\text{OH} \xrightarrow{\text{HA, heat}} \text{ major} + \text{ minor}$ rearrangement $\text{(-H}_2\text{O)}$</td>
</tr>
<tr>
<td>(e)</td>
<td>$\text{OH} \xrightarrow{\text{HA, heat}} \text{ major} + \text{ minor}$ $\text{(-H}_2\text{O)}$</td>
</tr>
</tbody>
</table>

**Reactions:**

- **Hydride Shift:** $\text{OH} \xrightarrow{\text{HA}} \text{OH}_2^+ \xrightarrow{\text{H}_2\text{O}} \text{ major product}$ (may be concerted with departure of the leaving group) 
- **Methanide Shift:** $\text{OH} \xrightarrow{\text{HA}} \text{OH}_2 \xrightarrow{\text{H}_2\text{O}} \text{ major product}$
124 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

(c) A methanide shift occurs.

(d) The required anti coplanar transition state leads only to \((E)\) alkene:

Index of Hydrogen Deficiency

7.45 (a) Caryophyllene has the same molecular formula as zingiberene (Review Problem 4.21); thus it, too, has an index of hydrogen deficiency equal to 4. That 1 mol of caryophyllene absorbs 2 mol of hydrogen on catalytic hydrogenation indicates the presence of two double bonds per molecule.

(b) Caryophyllene molecules must also have two rings. (See Review Problem 23.2 for the structure of caryophyllene.)

7.46 (a) \(C_{30}H_{62}\) = formula of alkane
\(C_{30}H_{50}\) = formula of squalene
\(H_D\) = difference = 6 pairs of hydrogen atoms
Index of hydrogen deficiency = 6

(b) Molecules of squalene contain six double bonds.

(c) Squalene molecules contain no rings. (See Review Problem 23.2 for the structural formula of squalene.)

Structure Elucidation

7.47 That \(I\) and \(J\) rotate plane-polarized light in the same direction tells us that \(I\) and \(J\) are not enantiomers of each other. Thus, the following are possible structures for \(I, J,\) and \(K\). (The enantiomers of \(I, J,\) and \(K\) would form another set of structures, and other answers are possible as well.)
ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

7.48 The following are possible structures:

7.49 Challenge Problems
7.50 (a) We are given (Section 7.3A) the following heats of hydrogenation:

\[
\begin{align*}
\text{cis-2-Butene} + \text{H}_2 & \xrightarrow{\text{Pt}} \text{butane} \quad \Delta H^\circ = -120 \text{ kJ mol}^{-1} \\
\text{trans-2-Butene} + \text{H}_2 & \xrightarrow{\text{Pt}} \text{butane} \quad \Delta H^\circ = -115 \text{ kJ mol}^{-1}
\end{align*}
\]

Thus, for cis-2-Butene \rightarrow trans-2-butene \quad \Delta H^\circ = -5.0 \text{ kJ mol}^{-1}

(b) Converting cis-2-butene into trans-2-butene involves breaking the \(\pi\) bond. Therefore, we would expect the energy of activation to be at least as large as the \(\pi\)-bond strength, that is, at least 264 kJ mol\(^{-1}\).

(c) \[
\Delta G^\circ = -5.0 \text{ kJ mol}^{-1}
\]

7.51 (a) With either the \((1R,2R)^-\) or the \((1S,2S)^-\)1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of the H- and Br-. In either case, the elimination leads only to \((Z)^-1\)-bromo-1,2-diphenylethene:

\[
\begin{align*}
(1R,2R)^-1,2\text{-Dibromo-1,2-diphenylethane} & \rightarrow (Z)^-1\text{-Bromo-1,2-diphenylethene} \\
& \quad \text{(anti coplanar orientation of H- and Br)}
\end{align*}
\]

\[
\begin{align*}
(1S,2S)^-1,2\text{-Dibromo-1,2-diphenylethane} & \rightarrow (Z)^-1\text{-Bromo-1,2-diphenylethene} \\
& \quad \text{(anti coplanar orientation of H- and Br)}
\end{align*}
\]
(b) With (1R,2S)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of the H- and Br-. In either case, the elimination leads only to (E)-1-bromo-1,2-diphenylethene:

(1R,2S)-1,2-Dibromo-1,2-diphenylethane (anti coplanar orientation of H and Br)

(c) With (1R,2S)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of both bromine atoms. In this case, the elimination leads only to (E)-1,2-diphenylethene:

(1R,2S)-1,2-Dibromo-1,2-diphenylethane (anti coplanar orientation of both -Br atoms)

7.52 (a) 

(b) No, tetrasubstituted double bonds usually show no C= C stretching absorption in their infrared spectra.

7.53

7.54 (a) Three
(b) Six
QUIZ

7.1 Which conditions/reagents would you employ to obtain the best yields in the following reaction?

\[
\begin{align*}
\text{(a) } & \text{H}_2\text{O}/\text{heat} & \text{(c) } & \text{OK} / \text{OH}, \text{heat} \\
\text{(b) } & \text{ONa} / \text{OH} & \text{(d) } & \text{Reaction cannot occur as shown}
\end{align*}
\]

7.2 Which of the following names is incorrect?

(a) 1-Butene (b) trans-2-Butene (c) \((Z)-2\)-Chloro-2-pentene (d) 1,1-Dimethylcyclopentene (e) Cyclohexene

7.3 Select the major product of the reaction

\[
\begin{align*}
\text{(a) } & \text{(c) } & \text{(e) }
\end{align*}
\]
7.4 Supply the missing reagents.

(a)  
(b)  
(c)  
(d)  
(e)  

7.5 Arrange the following alkenes in order of decreasing stability: 1-Pentene, cis-2-pentene, trans-2-pentene, 2-methyl-2-butene.

Most stable  >  >  >  Least stable

7.6 Complete the following synthesis.

(a)  
(b)  
(c)  
(d)  
(e)  

2-Pentyne