

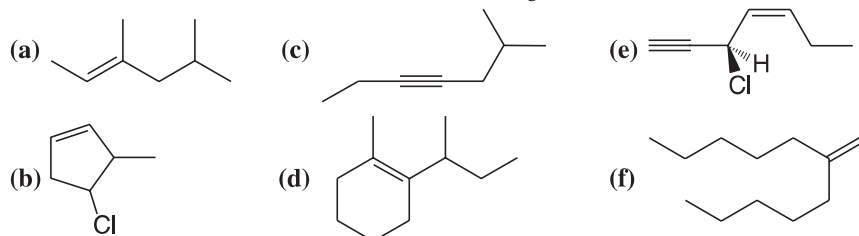
7.26 Write a structural formula for each of the following:

- | | | |
|----------------------------|--|--|
| (a) 3-Methylcyclobutene | (e) (<i>E</i>)-2-Pentene | (i) (<i>Z</i>)-1-Cyclopropyl-1-pentene |
| (b) 1-Methylcyclopentene | (f) 3,3,3-Tribromopropene | (j) 5-Cyclobutyl-1-pentene |
| (c) 2,3-Dimethyl-2-pentene | (g) (<i>Z,4R</i>)-4-Methyl-2-hexene | (k) (<i>R</i>)-4-Chloro-2-pentyne |
| (d) (<i>Z</i>)-3-Hexene | (h) (<i>E,4S</i>)-4-Chloro-2-pentene | (l) (<i>E</i>)-4-Methylhex-4-en-1-yne |

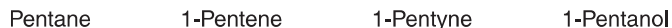
7.27 Write three-dimensional formulas for and give names using (*R*)-(*S*) and (*E*)-(*Z*) designations for the isomers of:

- | | |
|----------------------------|------------------------------------|
| (a) 4-Bromo-2-hexene | (c) 2,4-Dichloro-2-pentene |
| (b) 3-Chloro-1,4-hexadiene | (d) 2-Bromo-4-chlorohex-2-en-5-yne |

7.28 Give the IUPAC names for each of the following:



7.29 Without consulting tables, arrange the following compounds in order of decreasing acidity:



SYNTHESIS

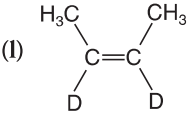
7.30 Outline a synthesis of propene from each of the following:

- | | | |
|------------------------|-----------------------|------------------------|
| (a) Propyl chloride | (c) Propyl alcohol | (e) 1,2-Dibromopropane |
| (b) Isopropyl chloride | (d) Isopropyl alcohol | (f) Propyne |

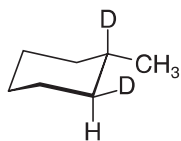
7.31 Outline a synthesis of cyclopentene from each of the following:

- | | |
|-----------------------|-------------------|
| (a) Bromocyclopentane | (b) Cyclopentanol |
|-----------------------|-------------------|

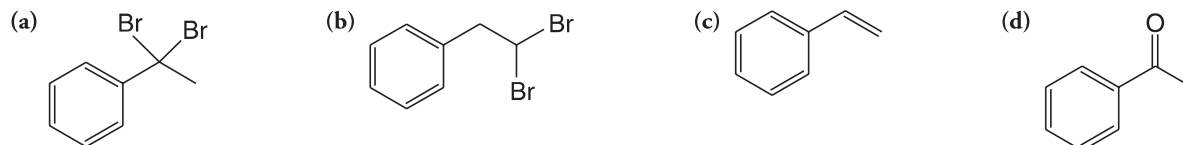
7.32 Starting with ethyne, outline syntheses of each of the following. You may use any other needed reagents, and you need not show the synthesis of compounds prepared in earlier parts of this problem.

- | | | |
|----------------------------|---------------------------|---|
| (a) Propyne | (f) 1-Pentyne | (k) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CD}$ |
| (b) 1-Butyne | (g) 2-Hexyne | (l)  |
| (c) 2-Butyne | (h) (<i>Z</i>)-2-Hexene | |
| (d) <i>cis</i> -2-Butene | (i) (<i>E</i>)-2-Hexene | |
| (e) <i>trans</i> -2-Butene | (j) 3-Hexyne | |

7.33 Starting with 1-methylcyclohexene and using any other needed reagents, outline a synthesis of the following deuterium-labeled compound:

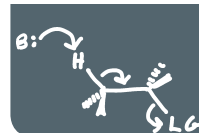


7.34 Outline a synthesis of phenylethyne from each of the following:

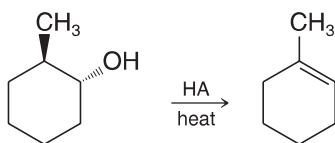


DEHYDROHALOGENATION AND DEHYDRATION

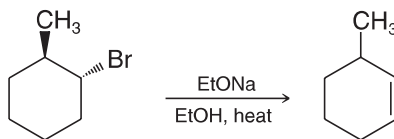
7.35 Write a three-dimensional representation for the transition state structure leading to formation of 2-methyl-2-butene from reaction of 2-bromo-2-methylbutane with sodium ethoxide.



7.36 When *trans*-2-methylcyclohexanol (see the following reaction) is subjected to acid-catalyzed dehydration, the major product is 1-methylcyclohexene:

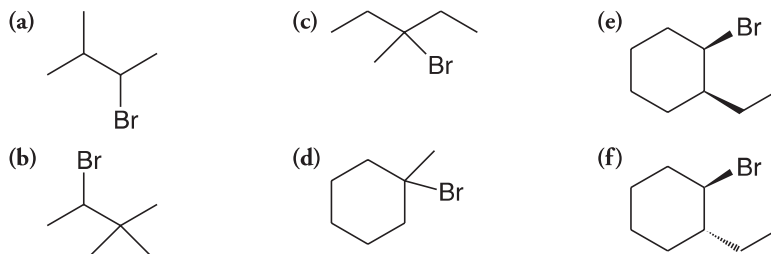


However, when *trans*-1-bromo-2-methylcyclohexane is subjected to dehydrohalogenation, the major product is 3-methylcyclohexene:

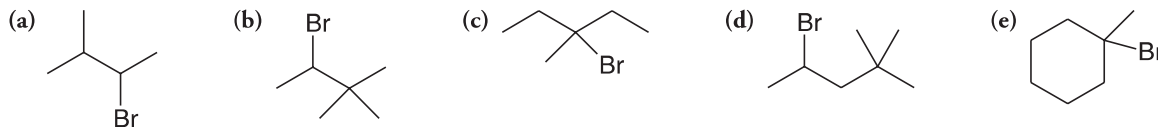


Account for the different products of these two reactions.

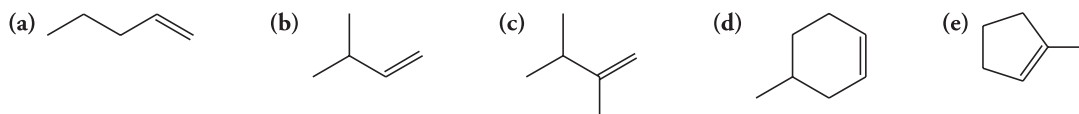
7.37 Write structural formulas for all the products that would be obtained when each of the following alkyl halides is heated with sodium ethoxide in ethanol. When more than one product results, you should indicate which would be the major product and which would be the minor product(s). You may neglect *cis*–*trans* isomerism of the products when answering this question.



7.38 Write structural formulas for all the products that would be obtained when each of the following alkyl halides is heated with potassium *tert*-butoxide in *tert*-butyl alcohol. When more than one product results, you should indicate which would be the major product and which would be the minor product(s). You may neglect *cis*–*trans* isomerism of the products when answering this question.



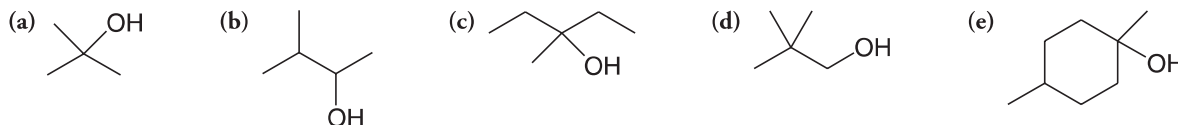
7.39 Starting with an appropriate alkyl halide and base, outline syntheses that would yield each of the following alkenes as the major (or only) product:



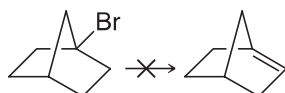
7.40 Arrange the following alcohols in order of their reactivity toward acid-catalyzed dehydration (with the most reactive first):

1-Pentanol 2-Methyl-2-butanol 3-Methyl-2-butanol

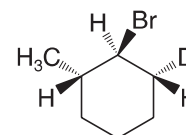
7.41 Give the products that would be formed when each of the following alcohols is subjected to acid-catalyzed dehydration. If more than one product would be formed, designate the alkene that would be the major product. (Neglect *cis*–*trans* isomerism.)



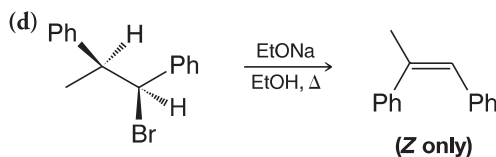
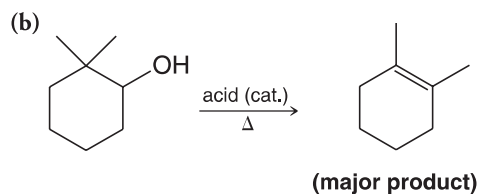
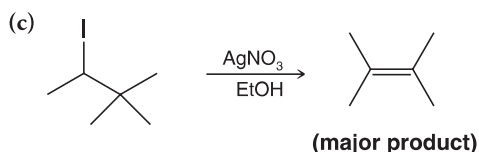
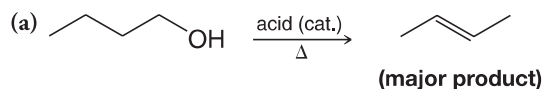
7.42 1-Bromobicyclo[2.2.1]heptane does not undergo elimination (below) when heated with a base. Explain this failure to react. (Construction of molecular models may help.)



7.43 When the deuterium-labeled compound shown at right is subjected to dehydrohalogenation using sodium ethoxide in ethanol, the only alkene product is 3-methylcyclohexene. (The product contains no deuterium.) Provide an explanation for this result.

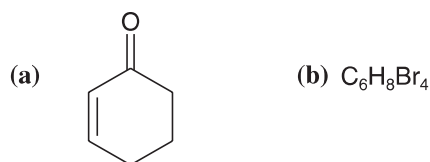


7.44 Provide a mechanistic explanation for each of the following reactions:



INDEX OF HYDROGEN DEFICIENCY

7.45 What is the index of hydrogen deficiency (IHD) (degree of unsaturation) for each of the following compounds?



7.46 Caryophyllene, a compound found in oil of cloves, has the molecular formula $C_{15}H_{24}$ and has no triple bonds. Reaction of caryophyllene with an excess of hydrogen in the presence of a platinum catalyst produces a compound with the formula $C_{15}H_{28}$. How many (a) double bonds and (b) rings does a molecule of caryophyllene have?

7.47 Squalene, an important intermediate in the biosynthesis of steroids, has the molecular formula $C_{30}H_{50}$ and has no triple bonds.

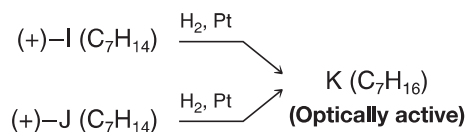
(a) What is the index of hydrogen deficiency of squalene?

(b) Squalene undergoes catalytic hydrogenation to yield a compound with the molecular formula $C_{30}H_{62}$. How many double bonds does a molecule of squalene have?

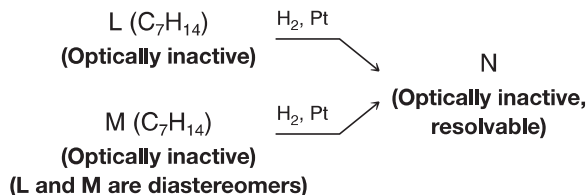
(c) How many rings?

STRUCTURE ELUCIDATION

7.48 Compounds **I** and **J** both have the molecular formula C_7H_{14} . Compounds **I** and **J** are both optically active and both rotate plane-polarized light in the same direction. On catalytic hydrogenation **I** and **J** yield the same compound **K** (C_7H_{16}). Compound **K** is optically active. Propose possible structures for **I**, **J**, and **K**.

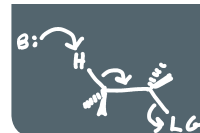


7.49 Compounds **L** and **M** have the molecular formula C_7H_{14} . Compounds **L** and **M** are optically inactive, are nonresolvable, and are diastereomers of each other. Catalytic hydrogenation of either **L** or **M** yields **N**. Compound **N** is optically inactive but can be resolved into separate enantiomers. Propose possible structures for **L**, **M**, and **N**.



CHALLENGE PROBLEMS

7.50 Propose structures for compounds **E–H**. Compound **E** has the molecular formula C_5H_8 and is optically active. On catalytic hydrogenation **E** yields **F**. Compound **F** has the molecular formula C_5H_{10} , is optically inactive, and cannot be resolved into separate enantiomers. Compound **G** has the molecular formula C_6H_{10} and is optically active. Compound **G** contains no triple bonds. On catalytic hydrogenation **G** yields **H**. Compound **H** has the molecular formula C_6H_{14} , is optically inactive, and cannot be resolved into separate enantiomers.

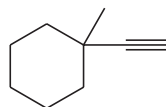


7.51 Consider the interconversion of *cis*-2-butene and *trans*-2-butene.

- (a) What is the value of ΔH° for the reaction *cis*-2-butene \rightarrow *trans*-2-butene (see Section 7.3A)?
 (b) Assume $\Delta H^\circ \cong \Delta G^\circ$. What minimum value of ΔG^\ddagger would you expect for this reaction (see Section 1.13A)?
 (c) Sketch a free-energy diagram for the reaction and label ΔG° and ΔG^\ddagger .

7.52 (a) Partial dehydrohalogenation of either (1*R*,2*R*)-1,2-dibromo-1,2-diphenylethane or (1*S*,2*S*)-1,2-dibromo-1,2-diphenylethane enantiomers (or a racemate of the two) produces (*Z*)-1-bromo-1,2-diphenylethane as the product, whereas (b) partial dehydrohalogenation of (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane (the meso compound) gives only (*E*)-1-bromo-1,2-diphenylethane. (c) Treating (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane with sodium iodide in acetone produces only (*E*)-1,2-diphenylethane. Explain these results.

7.53 (a) Using reactions studied in this chapter, show steps by which this alkyne could be converted to the seven-membered ring homolog of the product obtained in Problem 7.44(b).



(b) Could the homologous products obtained in these two cases be relied upon to show infrared absorption in the 1620–1680-cm⁻¹ region?

7.54 Predict the structures of compounds **A**, **B**, and **C**:

A is an unbranched C₆ alkyne that is also a primary alcohol.

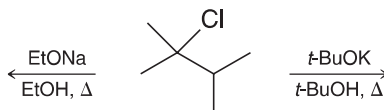
B is obtained from **A** by use of hydrogen and nickel boride catalyst or dissolving metal reduction.

C is formed from **B** on treatment with aqueous acid at room temperature. Compound **C** has no infrared absorption in either the 1620–1680-cm⁻¹ or the 3590–3650-cm⁻¹ region. It has an index of hydrogen deficiency of 1 and has one chirality center but forms as the racemate.

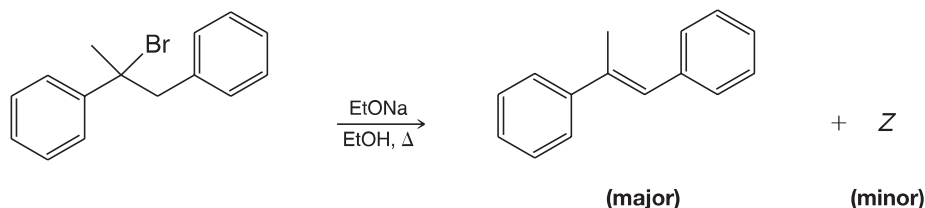
7.55 What is the index of hydrogen deficiency for (a) C₇H₁₀O₂ and (b) C₅H₄N₄?

LEARNING GROUP PROBLEMS

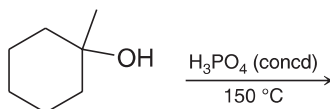
1. Write the structure(s) of the major product(s) obtained when 2-chloro-2,3-dimethylbutane (either enantiomer) reacts with (a) sodium ethoxide (EtONa) in ethanol (EtOH) at 80 °C or (in a separate reaction) with (b) potassium *tert*-butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH) at 80 °C. If more than one product is formed, indicate which one would be expected to be the major product. (c) Provide a detailed mechanism for formation of the major product from each reaction, including a drawing of the transition state structures.



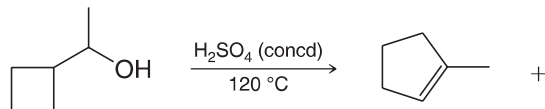
2. Explain using mechanistic arguments involving Newman projections or other three-dimensional formulas why the reaction of 2-bromo-1,2-diphenylpropane (either enantiomer) with sodium ethoxide (EtONa) in ethanol (EtOH) at 80 °C produces mainly (*E*)-1,2-diphenylpropene [little of the (*Z*) diastereomer is formed].



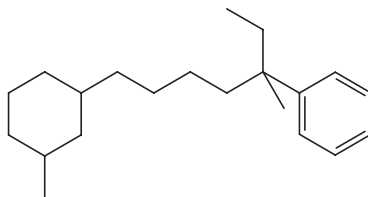
3. (a) Write the structure of the product(s) formed when 1-methylcyclohexanol reacts with 85% (concd) H₃PO₄ at 150 °C. (b) Write a detailed mechanism for the reaction.



4. Consider the reaction of 1-cyclobutylethanol (1-hydroxyethylcyclobutane) with concentrated H_2SO_4 at 120°C . Write structures of all reasonable organic products. Assuming that methylcyclopentene is one product, write a mechanism that accounts for its formation. Write mechanisms that account for formation of all other products as well.



5. Consider the following compound:



- Develop all reasonable retrosynthetic analyses for this compound (any diastereomer) that, at some point, involve carbon–carbon bond formation by alkylation of an alkynide ion.
- Write reactions, including reagents and conditions, for syntheses of this compound that correspond to the retrosynthetic analyses you developed above.
- Infrared spectroscopy could be used to show the presence of certain impurities in your final product that would result from leftover intermediates in your syntheses. Which of your synthetic intermediates would show IR absorptions that are distinct from those in the final product, and in what regions of the IR spectrum would the absorptions occur?
- Draw a three-dimensional structure for either the *cis* or *trans* form of the target molecule. Use dashed and solid wedges where appropriate in the alkyl side chain and use a chair conformational structure for the ring. (*Hint*: Draw the structure so that the carbon chain of the most complicated substituent on the cyclohexane ring and the ring carbon where it is attached are all in the plane of the paper. In general, for three-dimensional structures choose an orientation that allows as many carbon atoms as possible to be in the plane of the paper.)