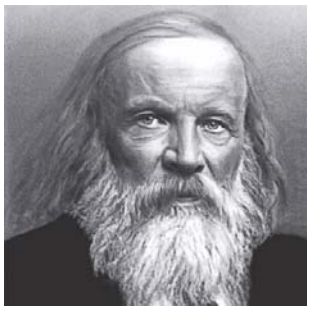
Exercise 14

Thought Provoking Problems

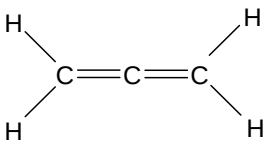
Fig. X14-1



Dimitri Mendeleev (1834 - 1907)
By developing the periodic table, Mendeleev solved one of the most thought provoking problems of chemistry.
http://www.chem.msu.su/eng/misc/mendeleev/
http://web.lemoyne.edu/~giunta/mendel.html
http://www.woodrow.org/teachers/chemistry/institutes/1992/Mendeleev.html

To become competent in the field of organic chemistry, you need to accumulate a significant knowledge base of the reactions and concepts and develop the ability to use the knowledge to solve problems. Your textbook is loaded with problems that are the key to the learning of organic chemistry. You will learn organic chemistry by doing the problems. Some problems primarily involve recall but other problems require an understanding of the mechanism of a reaction and/or the use of reasoning to determine the probable solution. While the addition of bromine to ethylene is primarily a recall exercise, the addition of bromine to cyclohexene requires that you know that the mechanism involves an anti addition and therefore should yield trans-1,2-dibromocyclohexane. It is important to note the word *should* in the previous sentence because your text presents generalizations and we often find in organic chemistry that specific reactions, unless run under exactly the right conditions, can give results that differ significantly from our expectations. Since there are a plethora of problems in your textbook, this exercise section does not attempt to provide an alternative set of exercises. However, this exercise is included to provide examples of problems that require the use of not just the recall of reaction products but also the application of the many concepts that enable you to predict outcomes in new situations. These problems are not necessarily original and appear in many texts in one form or another. They are offered here as a method for you to review organic chemistry and to help you achieve competency in organic chemistry. For thought provoking problems involving acid base concepts, see ***Exercise 6***. For examples of synthetic problems, see your textbook and ***Exercise 12***. Please note that the last four problems below do not involve traditional organic chemistry but fit the description of the title of this exercise.

1. 1,2-Propadiene, also called allene, is the parent compound of a rare and here-to-fore rather neglected class of compounds that contain cumulated π bonds.

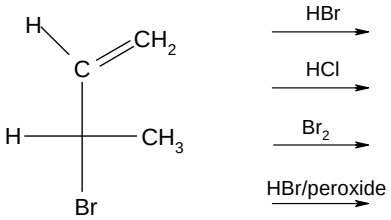


   a. Allenes do provide an interesting application of hybridization models to the determination of geometry. Are the hydrogens on the left co-planar with the hydrogens on the right? Explain your reasoning.

   b. The heats of hydrogenation of 2,3-pentadiene, 1,4-pentadiene and 1,3-pentadiene are -295.0, -251.9 and -226.4 kJ/mol respectively. Rank these compounds from most stable to least stable and explain the ranking.

   c. The mirror images of 2,3-pentadiene are not superimposable and therefore the molecule is chiral. Explain how 2,3-pentadiene can be chiral.

2. Answer the questions below for each of the addition reactions listed:



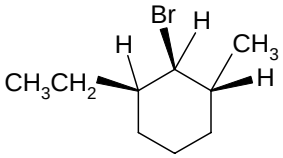
   a. Assuming Markovnikov's rule is appropriately applied, how many products could be separated from the product mixture? Assume that it is possible to separate all compounds except enantiomers.

   b. How many of the fractions are optically active?

3. a. Give the products of the hydrobromination (1 mol) of 2-methyl-1,3-butadiene at relatively low temperature and relatively high temperature.

   b. Give the favored position for protonation of 1,3,5 hexatriene in the first step of the addition of one mole of HBr to the compound. Explain your answer.

4.



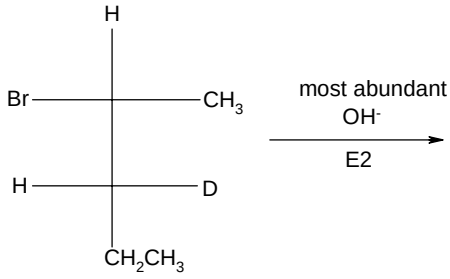
   a. $\xrightarrow[\text{E2}]{\text{OH}^-/\text{ROH}}$

   b. $\xrightarrow[S_N1]{\text{OH}^-}$

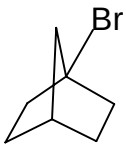
   c. $\xrightarrow[S_N2]{\text{OH}^-}$

   d. $\xrightarrow[\text{E1}]{\text{OH}^-}$

5.



6. Why is the compound to the right unreactive in both substitution and elimination reactions? Be sure to consider S_N1, S_N2, E1 and E2 mechanisms.



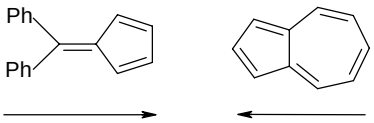
7. The free radical chlorination of hydrocarbons to introduce a functional group into the hydrocarbon has two very significant problems associated with the process. Since chlorine radicals are very reactive, they are not very selective so mixtures result if there is more than one kind of hydrogen present in the hydrocarbon. Second, once some product is formed, there is a tendency for the product to undergo chlorination resulting in a complex mixture of polychlorinated products.

   a. Assuming that the chlorination can be stopped after one substitution, in addition to methane and ethane, name at least two hydrocarbons that might be successfully monochlorinated.

   b. For the monochlorination of *(S)*-2-chlorobutane:
      1. How many isomers could be detected using gas chromatography (assume all isomers except enantiomers can be separated)?
      2. How many of the fractions should be optically active?

8. (R)-1-Fluoro-2-propanol $\xrightarrow{TsCl}$ $\xrightarrow{CN^-}$

9. The dipole moments of diphenylfulvene and azulene are illustrated in the figure to the right. The head of the arrow represents the negative end of the dipole. Account for the dipoles and their directions.



10. Give the expected products for the reaction of styrene (phenylethene) with bromine with iron(III) bromide present as a catalyst. In other words, should ortho/para or meta substitution dominate? Use resonance structures for the intermediates produced by substitution in each position on the ring to support your answer.

11. Benzene and perdeuterobenzene undergo nitration at the same rate. What conclusions can you draw from this information about the mechanism of the reaction?

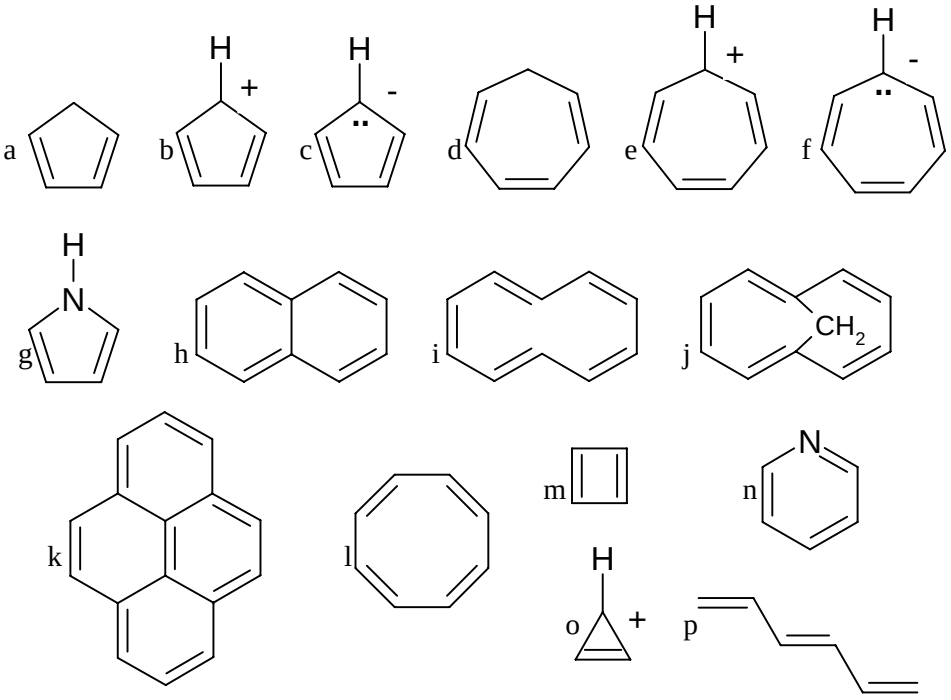
12. 2-butanone $\xrightarrow{NaBD_4}$ $\xrightarrow{H^+/H_2O}$

13. An optically active compound (A) with an *R* configuration and the formula C_6H_{12} reacts with 1 mole of H_2/Pt to give C_6H_{14} (B). B is not optically active. Ozonolysis of A yields formaldehyde and C. Give the structures of A, B and C.

14. a. When acetic acid is esterified in acid medium with ethanol with the ethanolic oxygen enriched with oxygen-18, the ethyl acetate obtained has the same percentage of labeled oxygen as the original ethanol had. Explain the mechanistic implications of this result.

    b. When a partial esterification of acetic acid is run in water enriched in oxygen-18, recovered "unreacted" acetic is found to contain an enrichment of oxygen-18 at both oxygens. What conclusions regarding the mechanism can be drawn from this result?

15. Which of the following molecules and ions are aromatic? Explain your answers.



16. An optically active compound, A, with the formula C_8H_{16} and an ir absorption at about 1670 cm^{-1} undergoes ozonolysis to yield an optically active aldehyde and an inactive ketone. What is the structure of A?

17. Another optically active compound, B, with the formula C_8H_{16} undergoes hydrogenation to yield an inactive product. Give the structures of all the possible products and suggest methods for distinguishing among them.

18. A compound (C) with the formula C_8H_{10} reacts with Br_2 with a catalyst to give 3 isomers with the formula C_8H_9Br. Give the structure of C.

19. Some analytical instruments perform functions similar to those performed by human senses. Compare the performance of the instruments to the human senses. Which has greater sensitivity? Are there human senses not duplicated by instruments and vice versa? Should it be possible to develop an instrument for any human sense not currently duplicated by an instrument?

20. The electromagnetic radiation spectrum extends far beyond the region of sensitivity of the human eye both to lower and higher energies. Suggest reasons why animals did not evolve with a wider range of sensitivity? Consider in your response the type of detector that is needed as a function of energy and types of energy transitions that are active in particular energy regions.

21. The extraterrestrial intelligent life portrayed in science fantasy movies often bears some resemblance to humans. Is this likely or does this demonstrate the limits of human imagination? Explain your answer. Be sure to consider senses, intelligence and modes of movement, manipulation and reproduction.

22. Explain whether life could be based on substances other than water, oxygen and carbon polymers.