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Study Guide and Solutions Manual

Organic Chemistry A Short Course

THIRTEENTH EDITION

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Introduction to the Student

This study guide and solutions book was written to help you learn organic chemistry. The principles and facts of this subject are not easily learned by simply reading them, even repeatedly. Formulas, equations, and molecular structures are best mastered by *written* practice. To help you become thoroughly familiar with the material, we have included many problems within and at the end of each chapter in the text.

It is our experience that such questions are not put to their best use unless correct answers are also available. Indeed, answers alone are not enough. If you know how to work a problem and find that your answer agrees with the correct one, fine. But what if you work conscientiously, yet cannot solve the problem? You then give in to temptation, look up the answer, and encounter yet another dilemma—how in the world did the author get that answer? This solutions book has been written with this difficulty in mind. For many of the problems, all of the reasoning involved in getting the correct answer is spelled out in detail. Many of the answers also include cross-references to the text. If you cannot solve a particular problem, these references will guide you to parts of the text that you should review.

Each chapter of the text is briefly summarized. Whenever pertinent, the chapter summary is followed by a list of all the new reactions and mechanisms encountered in that chapter. These lists should be especially helpful to you as you review for examinations.

When you study a new subject, it is always useful to know what is expected. To help you, we have included in this study guide a list of learning objectives for each chapter—that is, a list of what you should be able to do after you have read and studied that chapter. Your instructor may want to delete items from these lists of objectives or add to them. However, we believe that if you have mastered these objectives—and the problems should help you to do this—you should have no difficulty with examinations. Furthermore, you should be very well prepared for further courses that require this course as a prerequisite.

Near the end of this study guide you will find additional sections that may help you to study for the final examination in the course. The SUMMARY OF SYNTHETIC METHODS lists the important ways to synthesize each class of compounds discussed in the text. It is followed by the SUMMARY OF REACTION MECHANISMS. Both of these sections have references to appropriate portions of the text, in case you feel that further review is necessary. Finally, you will find two lists of sample test questions. The first deals with synthesis, and the second is a list of multiple-choice questions. Both of these sets should help you prepare for examinations.

In addition, we offer you a brief word of advice about how to learn the many reactions you will study during this course. First, learn the nomenclature systems thoroughly for each new class of compounds that is introduced. Then, rather than memorizing the particular examples of reactions given in the text, study reactions as being typical of a class of compounds. For example, if you are asked how compound A will react with compound B, proceed in the following way. First ask yourself: to what class of compounds does A belong? How does this class of compounds react with B (or with compounds of the general class to which B belongs)? Then proceed from the general reaction to the specific case at hand. This approach will probably help you to eliminate some of the memory work often associated with organic chemistry courses. We urge you to study regularly, and hope that this study guide and solutions book will make it easier for you to do so.

Great effort has been expended to ensure the accuracy of the answers in this book and we wish to acknowledge the helpful comments provided by David Ball (Cleveland State University) in this regard. It is easy for errors to creep in, however, and we will be particularly grateful to anyone who will call them to our attention. Suggestions for improving the book will also be welcome. Send them to:

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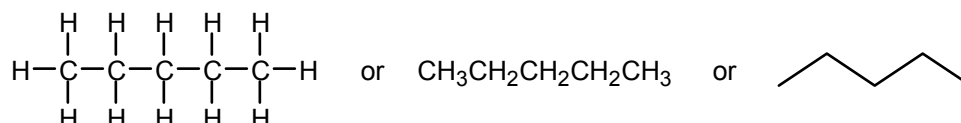
Bonding and Isomerism

Chapter Summary*

An **atom** consists of a nucleus surrounded by **electrons** arranged in **orbitals**. The electrons in the outer shell, or the **valence electrons**, are involved in bonding. **Ionic bonds** are formed by electron transfer from an **electropositive** atom to an **electronegative** atom. Atoms with similar electronegativities form **covalent bonds** by sharing electrons. A **single bond** is the sharing of one electron pair between two atoms. A covalent bond has specific **bond length** and **bond energy**.

Carbon, with four valence electrons, mainly forms covalent bonds. It usually forms four such bonds, and these may be with itself or with other atoms such as hydrogen, oxygen, nitrogen, chlorine, and sulfur. In pure covalent bonds, electrons are shared equally, but in **polar covalent bonds**, the electrons are displaced toward the more electronegative element. **Multiple bonds** consist of two or three electron pairs shared between atoms.

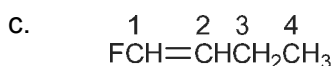
Structural (or **constitutional**) **isomers** are compounds with the same **molecular formulas** but different **structural formulas** (that is, different arrangements of the atoms in the molecule). **Isomerism** is especially important in organic chemistry because of the capacity of carbon atoms to be arranged in so many different ways: continuous chains, branched chains, and rings. Structural formulas can be written so that every bond is shown, or in various abbreviated forms. For example, the formula for *n*-pentane (*n* stands for normal) can be written as:



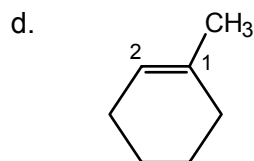
Some atoms, even in covalent compounds, carry a **formal charge**, defined as the number of valence electrons in the neutral atom minus the sum of the number of unshared electrons and half the number of shared electrons. **Resonance** occurs when we can write two or more structures for a molecule or ion with the same arrangement of atoms but different arrangements of the electrons. The correct structure of the molecule or ion is a **resonance hybrid** of the **contributing structures**, which are drawn with a double-headed arrow (\leftrightarrow) between them. Organic chemists use a curved arrow (\curvearrowright) to show the movement of an electron pair.

A **sigma (σ) bond** is formed between atoms by the overlap of two atomic orbitals along the line that connects the atoms. Carbon uses **sp^3 -hybridized orbitals** to form four such bonds. These bonds are directed from the carbon nucleus toward the corners of a tetrahedron. In **methane**, for example, the carbon is at the center and the four hydrogens are at the corners of a regular tetrahedron with H–C–H bond angles of 109.5° .

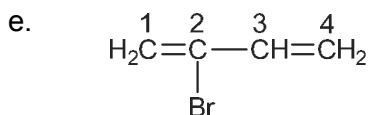
* In the chapter summaries, terms whose meanings you should know appear in boldface type.



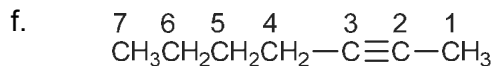
1-fluorobutene



1-methylcyclohexene

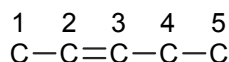


2-bromo-1,3-butadiene

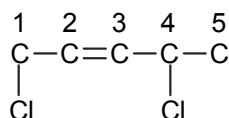


1-heptyne

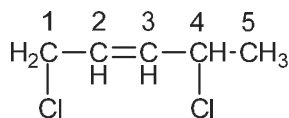
- 3.4 a. First write out the five-carbon chain, with a double bond between carbon-2 and carbon-3:



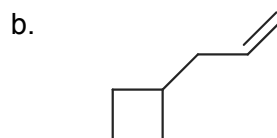
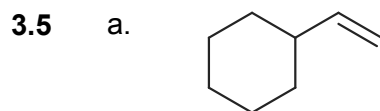
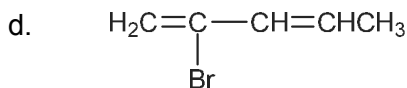
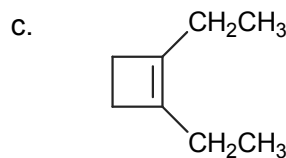
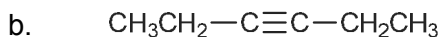
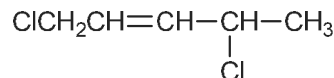
Add the substituents:



Fill in the hydrogens:



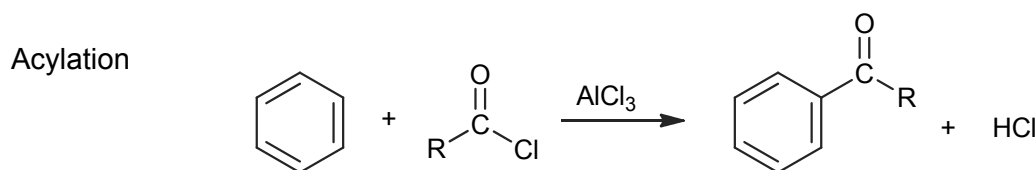
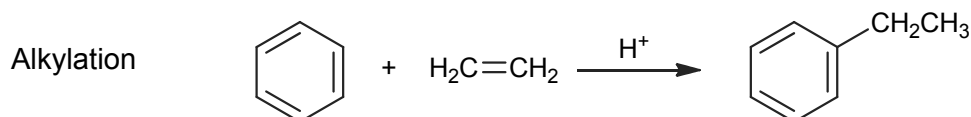
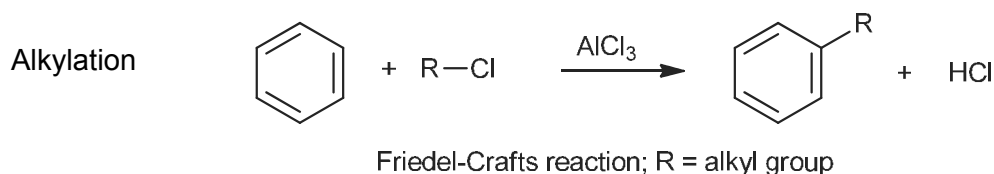
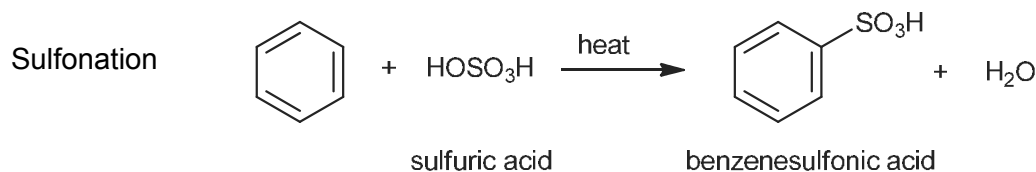
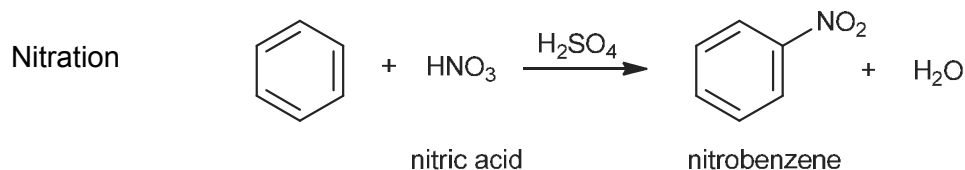
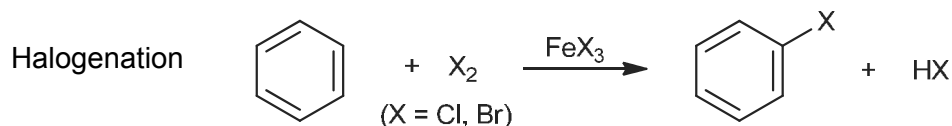
or



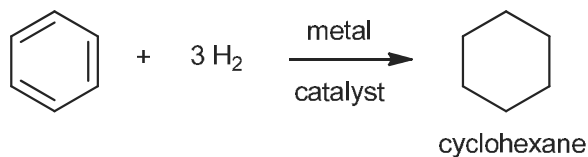
hexagonal rings separated by 3.4 Å. The **fullerenes** are a recently discovered novel polycyclic form of carbon.

Reaction Summary

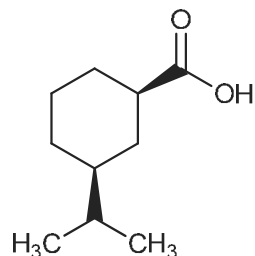
Electrophilic Aromatic Substitution



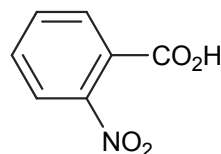
Catalytic Hydrogenation



10.3 a.



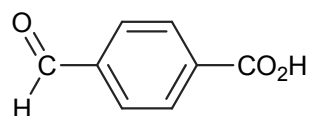
b.



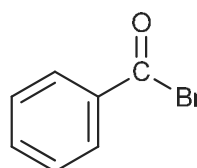
10.4 a. cyclopropanecarboxylic acid

b. *p*-methoxybenzoic acid

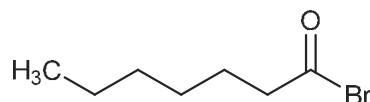
10.5 a.



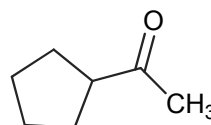
b.



c.



d.

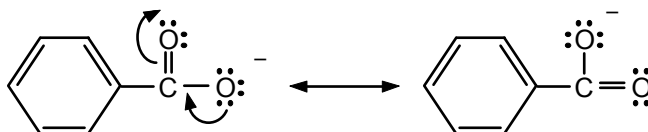


10.6 K_a is 1.8×10^{-5} for acetic acid and 5.0×10^{-2} for dichloroacetic acid. K_a is larger for dichloroacetic acid; it is the stronger acid. The ratio is:

$$\frac{5.0 \times 10^{-2}}{1.8 \times 10^{-5}} = 2.8 \times 10^3$$

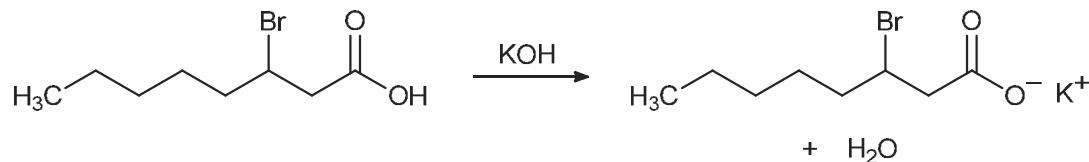
In other words, dichloroacetic acid is 2800 times stronger than acetic acid.

10.7 The negative charge in the benzoate anion cannot be delocalized into the aromatic, but can be distributed over the two oxygen atoms.



10.8 K_a for benzoic acid is 6.6×10^{-5} or 0.66×10^{-4} . For *o*-, *m*-, and *p*-chlorobenzoic acids, K_a is 12.5, 1.6, and 1.0×10^{-4} , respectively. All three chloro acids are stronger than benzoic acid. However, the difference is greatest for the ortho isomer since, in this isomer, the chloro substituent is closest to the carboxyl group and exerts the maximum electron-withdrawing inductive effect. The effect decreases as the distance between the chloro substituent and the carboxyl group increases.

10.9



10.10 The halide can be converted to the corresponding Grignard reagent, which can react with carbon dioxide to give the carboxylic acid.

Monosaccharides react with alcohols (H^+ catalyst) to give **glycosides**. The $-OH$ group at the anomeric carbon is replaced by an $-OR$ group. The product is an acetal. Alcohols and phenols often occur in nature combined with sugars as glycosides, which renders them water-soluble.

Disaccharides consist of two monosaccharides linked by a glycosidic bond between the anomeric carbon of one unit and a hydroxyl group (often on C-4) of the other unit. Examples include **maltose** and **cellobiose** (formed from two glucose units joined by a 1,4-linkage and differing only in configuration at the anomeric carbon, being α and β , respectively), **lactose** (from a galactose and glucose unit linked 1,4 and β), and **sucrose**, or cane sugar (from a fructose and glucose unit, linked at the anomeric carbon of each, or 1,2). Sugars such as fructose, glucose, and sucrose are sweet, but others (for example, lactose and galactose) are not. Some noncarbohydrates, such as **saccharin** and **aspartame**, also taste sweet.

Polysaccharides have many monosaccharide units linked by glycosidic bonds. **Starch** and **glycogen** are polymers of D-glucose, mainly linked 1,4 or 1,6 and α . **Cellulose** consists of D-glucose units linked 1,4 and β .

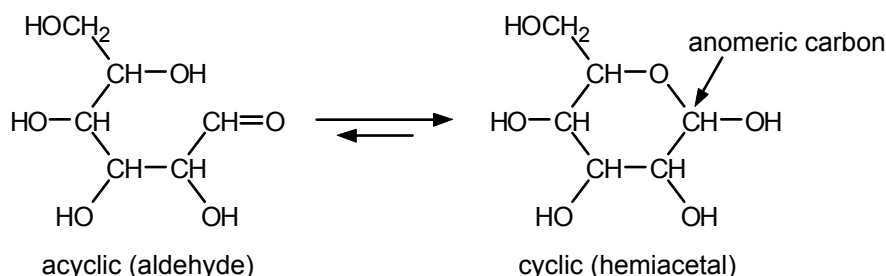
Monosaccharides with modified structures are often biologically important. Examples include **sugar phosphates**, **deoxy sugars**, **amino sugars**, and **ascorbic acid** (vitamin C).

Reaction Summary

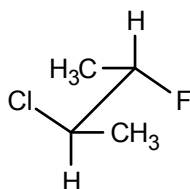
Hydrolysis



Acyclic and Cyclic Equilibration

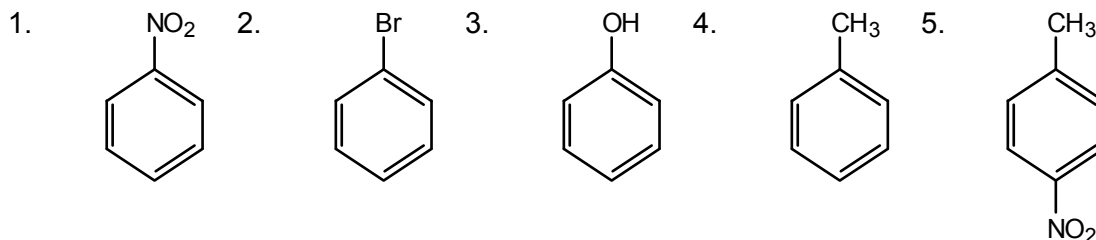


32. What is the correct name for the following compound?

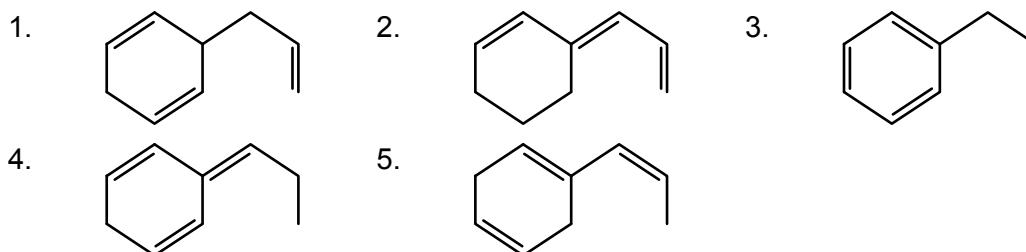


- | | |
|------------------------------------|------------------------------------|
| 1. (2R,3R)-2-chloro-3-fluorobutane | 2. (2R,3S)-2-chloro-3-fluorobutane |
| 3. (2S,3R)-2-chloro-3-fluorobutane | 4. (2S,3S)-2-chloro-3-fluorobutane |
| 5. none of the above | |

33. Which of the following compounds reacts least rapidly in electrophilic substitutions?



34. Which of the following compounds gives off the *least* amount of heat during hydrogenation?



35. The resonance contributor that is most important in the intermediate for *para* electrophilic substitution in toluene is:

