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# ORGANIC CHEMISTRY

## VOLUME II

Chemical Behavior of Organic Compounds  
and Multi-step Organic Synthesis

ROGER MACOMBER

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UNIVERSITY SCIENCE BOOKS COLLEGE OUTLINE SERIES

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# ORGANIC CHEMISTRY

## VOLUME II

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**Roger Macomber**

*Department of Chemistry  
University of Cincinnati*

University Science Books  
Sausalito, California

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# PREFACE

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In Volume I of this work we laid a foundation of concepts in the structure of organic molecules. We covered such topics as atomic structure, localized and delocalized chemical bonding, functional group recognition and nomenclature, molecular shape and stereochemistry, and properties of molecules. The final two chapters presented a general discussion of the thermodynamic and kinetic factors that control chemical reactions, the experimental techniques used to study reaction mechanisms, and a preview of the types of reactions and mechanisms to be encountered in this volume.

Now we are ready to examine the characteristic chemical behavior of each class of organic compounds, and because the chemical behavior of an organic compound is dictated primarily by the nature of the functional group(s) present, our foray into organic reactions will be arranged on the basis of functional group classes. Each of the first ten chapters will provide a synopsis of the reactions that a given functional group undergoes. At the end of each chapter, as part of the summary, there will be a list of all reactions and reagents encountered in that chapter. Then, in the final chapter, we will review these reactions from the perspective of synthesizing molecules by multi-step routes.

In writing this volume, I assumed that you have already mastered the concepts presented in Volume I. Nonetheless, I have included many references to the material in Volume I in case you feel the need to review it. These references are formatted in the following manner: (I.6-3) indicates Volume I, Chapter 6, Section 3. A reference such as (Section 6-3) indicates this volume, Chapter 6, Section 3.

You may notice that several topics covered in most contemporary organic chemistry textbooks are given relatively little attention here, while others are absent altogether. For example, our discussion of bioorganic chemistry is limited to the use of some bioorganic molecules as examples of reaction concepts. Polymer chemistry is mentioned briefly in two sections, and spectroscopic techniques, which were described briefly in I.7-2, are rarely mentioned in this volume. For those of you who will undertake further study in chemistry or biology, you will no doubt cover some of these topics in detail at a later time. On the other hand, if your formal chemistry studies are to end with organic chemistry, but you are still interested in some of these applications, you are encouraged to choose among the many introductory-level books on these topics. If you thoroughly learn the material presented in these two volumes, you will have mastered the fundamentals of organic chemistry on which these other applications are based!

Perhaps the single most important piece of advice I can give you is this: *DO THE PROBLEMS*. It is my conviction that more than half of the learning that you do in any chemistry course is a result of working the problems. As you begin reading this book, you will soon see that there are many examples and problems in each chapter, each with the answer appearing immediately after the question. You must develop enough discipline to try and work each problem *without looking at the answer!* Too many students read the question and the answer, then satisfy themselves that they could have arrived at the same answer. Do not adopt that approach. Work the problem yourself, and look at the answer only after you've given it your best shot. If your answer is not fully correct, you have missed something, and you should review the preceding material before going on.

But above all, the process of learning new things can be an exciting adventure. I have tried to write a book that will stimulate your curiosity and your thinking about organic chemistry. Now it's up to you to make the effort to expand your horizons. Good luck!

University of Cincinnati  
Cincinnati, Ohio

ROGER S. MACOMBER

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# ACKNOWLEDGMENTS

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This book would never have been more than an idea had it not been for the encouragement, advice, and able assistance of several very special people. Emily Thompson, Elinor Williams, and Susan McColl have my deep gratitude for bringing an earlier version of this book to fruition. Professors Al Pinhas (University of Cincinnati) and Marinus Bardolph (emeritus, Southern Illinois University) labored mightily over each detail in the manuscript and proofs. Every reader will benefit greatly from their careful reviews and suggestions. And because this book approaches organic chemistry somewhat differently than other mainstream textbooks on the subject, it required a publisher who has courage and confidence in this novel approach. This person is Bruce Armbruster, president of University Science Books, along with his most able editor, Jane Ellis.

Finally, I would like to express my gratitude to all my organic chemistry students and faculty colleagues at the University of Cincinnati over the past 27 years, who've given me the opportunity to develop my own philosophy of teaching organic chemistry.

*Cincinnati, Ohio*

ROGER S. MACOMBER

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# 1 SATURATED HYDROCARBONS

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## THIS CHAPTER IS ABOUT

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- ✓ Structural Considerations and Reactivity Patterns
  - ✓ Free-Radical Substitution
  - ✓ Stereochemistry and the Nature of Free Radicals
  - ✓ Pyrolysis and Cracking
  - ✓ Combustion and Its Consequences
  - ✓ Cycloalkanes with Small Rings
- 
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### 1-1. Structural Considerations and Reactivity Patterns

Saturated hydrocarbon molecules consist solely of C–C and C–H single bonds (I.5).<sup>\*</sup> Acyclic (non-cyclic) saturated hydrocarbons are called **alkanes** (I.5-1), and have molecular formula  $C_nH_{2n+2}$ . Cycloalkanes (I.5-4), hydrocarbon molecules with one or more rings, have molecular formula  $C_nH_{2n+2-2r}$ , where  $r$  is the number of rings (I.5-3). Collectively, these are known as **aliphatic compounds**.

Because C–C and C–H single bonds are both strong (I.9-1) and non-polar (I.2-6), alkanes and cycloalkanes are generally regarded as essentially non-polar compounds, and they tend to be relatively unreactive toward most polar chemical reagents and reaction conditions. Because they lack multiple bonds (I.2-5), saturated hydrocarbons cannot normally participate in pericyclic reactions (I.10-8). This leaves only free-radical reactions and certain high-temperature processes (e.g., pyrolysis and combustion) accessible to this class of compounds. On the other side of the coin, their low reactivity makes such compounds ideal for use as inert solvents (I.7-7) in organic reactions involving non-polar compounds.

The physical state of linear (I.5-1) alkanes at room temperature varies from gaseous (methane through butane) to liquid (pentane through heptadecane) to solid (octadecane and beyond). Their physical properties conform to expectations based on their molecular weight and weak intermolecular forces (I.7-7).

The hydrogens in typical alkanes and cycloalkanes have extremely low acidity, with  $pK_a$  values in the range 45–50 (I.10-3,4,5). Therefore, it is essentially impossible to find a base strong enough to deprotonate an alkane to give the corresponding carbanion (I.4-1). Instead, the usual approach to making such carbanions is an indirect one involving organometallic derivatives, as we shall see in Chapter 2. Similarly, because they lack  $\pi$ -bonds and non-bonding pairs, saturated hydrocarbons are extremely non-basic and cannot be protonated by even the strongest acids under most conditions. (There is evidence, however, that methane can be protonated *in the vapor phase* to give  $CH_5^+$ .)

There is one group of saturated hydrocarbons that *is* relatively reactive. This group includes the small-ring cycloalkanes such as cyclopropane, cyclobutane, and related bicyclic compounds (I.5-4), all of which possess considerable ring strain (I.7-3) that can be relieved in certain reactions.

With these generalizations as our guide, let's take a look at some of the few reactions that saturated hydrocarbons *do* undergo.

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<sup>\*</sup>Remember, this is Volume II of *Organic Chemistry*—you should have Volume I nearby, as we will refer to it fairly frequently, as is done here: “I.5” means Volume I, Chapter 5.

## 1-2. Free-Radical Substitution

The hydrogen atoms in alkanes, being terminal (univalent) atoms (I.3-1), are subject to **abstraction** by certain free radicals ( $R\cdot$ ).



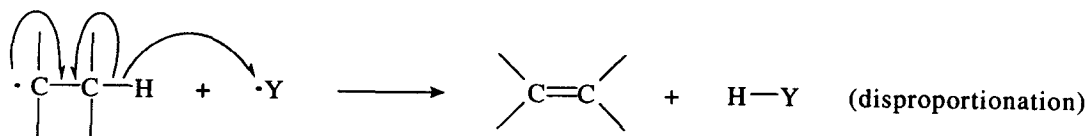
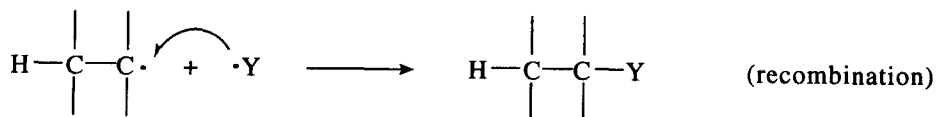
This type of reaction, which results in the formation of a new radical ( $\begin{array}{c} | \\ -C\cdot \\ | \end{array}$ ), was discussed in detail in I.10-6. For such an abstraction to take place, the new  $R-H$  bond must be at least as strong as the  $C-H$  bond being broken. Furthermore, the more stable the new radical is, the more readily it will be formed. For both these reasons, abstractions that lead to tertiary (I.5-2) or resonance-stabilized (I.4-3) radicals are preferred to those leading to secondary radicals, which in turn are more likely than those that give primary radicals.

The fate of the new radical usually involves its abstracting a terminal atom from another reactant molecule:

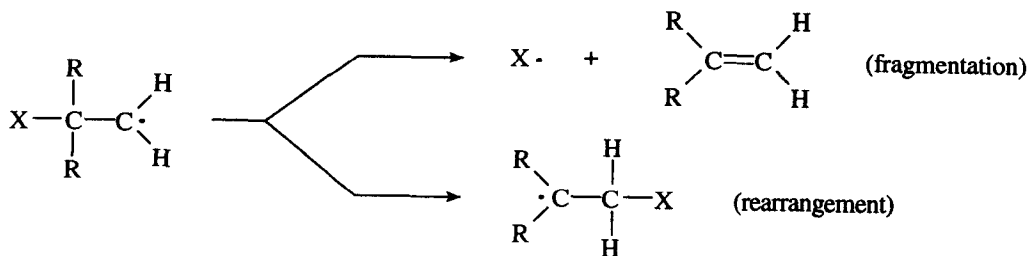


Often, the  $Y\cdot$  radical thereby generated can return to abstract a hydrogen from another molecule of the starting alkane, setting up a **chain reaction** mechanism (I.10-6). The tip-off that such a mechanism is occurring is the necessity for a free-radical initiator (I.10-6).

Instead of abstracting an atom, the new radical can sometimes undergo other processes such as **disproportionation** or **recombination** with another radical:



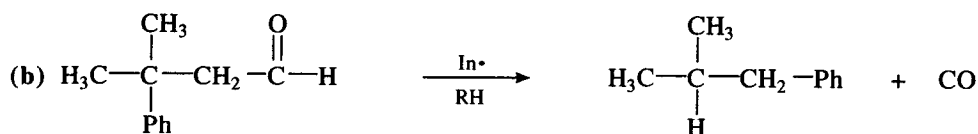
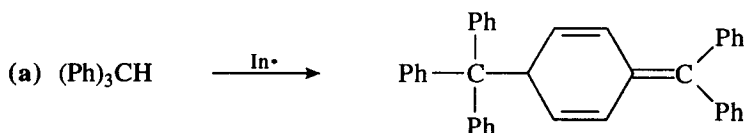
However, these processes are relatively improbable because of the very low concentrations of free radicals under most reaction conditions. Alternatively, the radical can undergo **fragmentation** or **rearrangement** if the product(s) is (are) more stable than initially formed radical. [The rearranged product is usually formed by a concerted (I.10-8) migration of  $X$ , rather than fragmentation followed by re-attachment of  $X\cdot$  at the less-substituted carbon.]



The biggest drawback to free-radical reactions is that free radicals are often not very selective in their reactions. That is, they can and do abstract all possible abstractable hydrogens (although

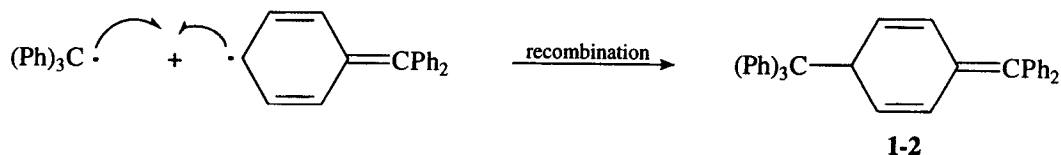
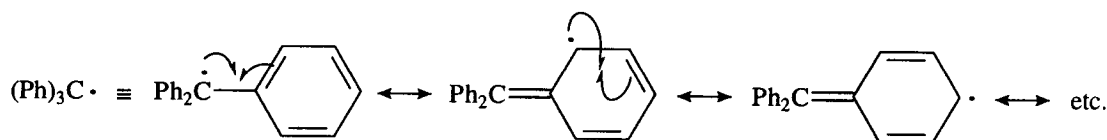
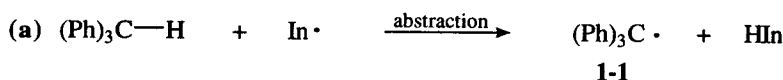
not in equal ratios), as well as undergoing many different fragmentations and rearrangements. Thus, free-radical reactions often give complex mixtures of products. The best free-radical reactions are those in which the reactant molecules have carefully selected structures designed to prefer just one type of free-radical process.

**EXAMPLE 1-1** Suggest a mechanism for each reaction below. Be sure to show each step in your mechanism.  $\text{In}\cdot$  represents the initiating radical (I.10-6),  $\text{RH}$  represents a source of readily abstractable hydrogens (e.g., the solvent), and  $\text{Ph}$  represents a phenyl group.

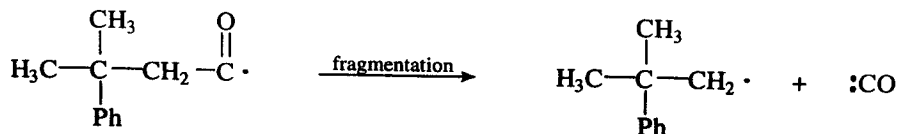
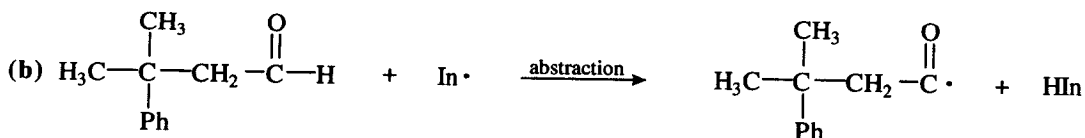


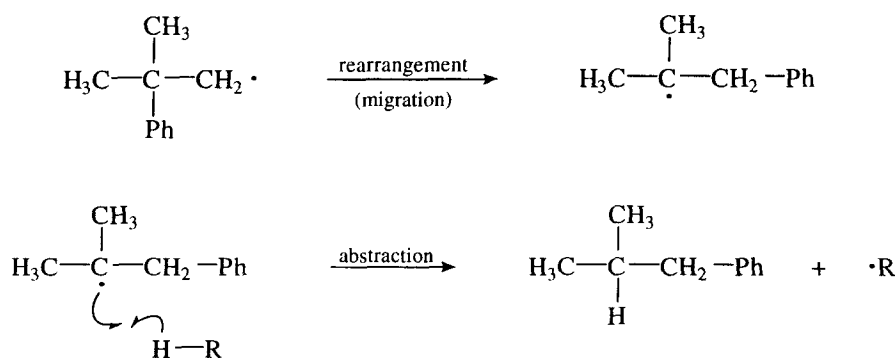
*Hint:* The aldehydic hydrogen is abstracted first.

**Solution**



Note that the triphenylmethyl radical (1-1) is highly stabilized by resonance (I.4), and is also sterically inhibited from recombination by the bulky phenyl groups. For this reason it forms the “head-to-tail” **dimer 1-2** (a molecule formed by the combination of two identical fragments) rather than the “head-to-head” dimer,  $(\text{Ph})_3\text{C}-\text{C}(\text{Ph})_3$ .





The driving force for the fragmentation is formation of the stable small molecule CO (carbon monoxide). The driving force for the rearrangement is formation of the more stable tertiary radical from the less stable primary one. It is also possible that the migration is concerted with (i.e., occurs at the same time as) the fragmentation. (The fate of  $\text{R}\cdot$ , which itself will lead to one or more side products, need not concern us at this point.)

**EXAMPLE 1-2** Explain why the 5-hexenyl radical cyclizes to the cyclopentylmethyl radical, even though both radicals are primary:

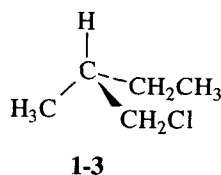


**Solution** This cyclization is thermodynamically driven because the new C–C  $\sigma$ -bond is stronger than the old C–C  $\pi$ -bond (I.9-1). Furthermore, the ring strain (I.7-3,5) in the five-membered ring is small and not sufficient to overcome the favorable bond strength driving force.

### 1-3. Stereochemistry and the Nature of Free Radicals

The stereochemical outcome of a reaction is often immensely valuable in sorting out its mechanistic details (I.8-10, I.10-8). Let's see what we can deduce about the properties of radicals by examining certain stereochemical facts. We'll begin with a review question.

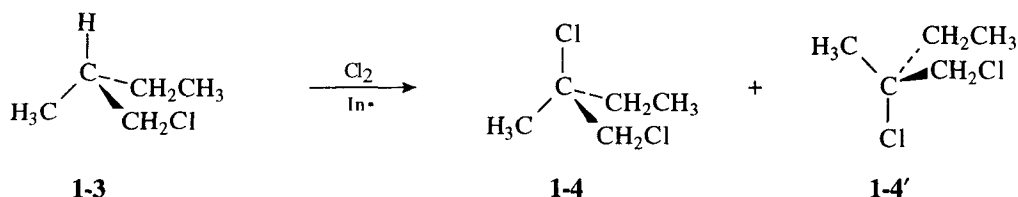
**EXAMPLE 1-3** (a) Give a complete name for structure 1-3. (b) Which hydrogen in 1-3 is most likely to undergo free-radical substitution? Why?



**Solution**

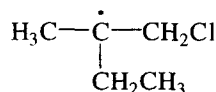
- (a) Structure 1-3 is the (R) enantiomer (I.8-4) of 1-chloro-2-methylbutane (I.6-3). The methine (number 2) carbon is the chiral center (I.8-3).  
 (b) The methine hydrogen, abstraction of which would lead to a tertiary radical, would be the most reactive toward free-radical substitution.

When compound 1-3 is subjected to free-radical chlorination, substitution takes place at the expected position. However, *two* products are formed in equal amounts, the two enantiomers of 1,2-dichloro-2-methylbutane (1-4):



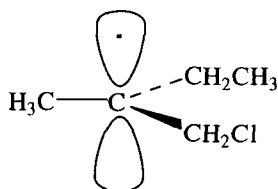
It can be easily demonstrated that both **1-4** and **1-4'** arise directly from **1-3**, i.e., that **1-4'** is *not* formed from **1-4**. We describe this result by saying that the reaction involves racemization (I.8-6) at the reaction center (the carbon at which substitution takes place). But how does this occur?

First of all, we must remember that the key intermediate in this reaction is the free radical (1-5) derived from 1-3.



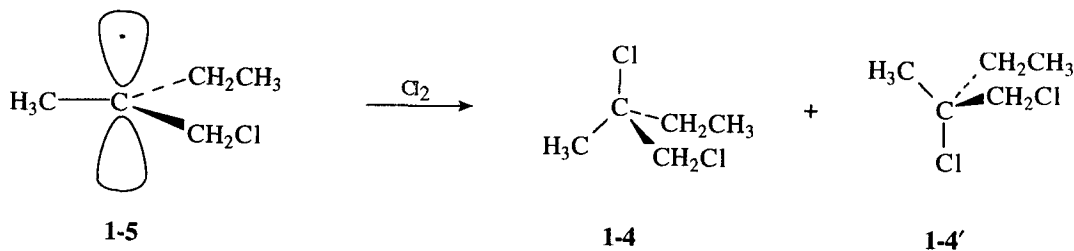
1-5

It is clear from the observed racemization that this radical must be able to react with  $\text{Cl}_2$  to give both enantiomers of the product in equal amounts. But what does this tell us about the nature of **1-5**? Because the free-radical carbon in **1-5** bears only three groups (or three and a half, if we count the unpaired electron as one half of a group), we would predict from VSEPR considerations (I.3-2) that it should be  $sp^2$  hybridized, or nearly so. This means that the three groups will lie in a (trigonal) plane, with the unpaired electron in a  $p$ -orbital perpendicular to the plane:



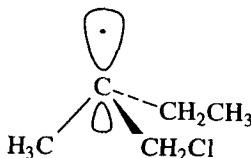
1-5

Once drawn this way, it is easy to see how a  $\text{Cl}_2$  molecule could attack either the upper or lower lobe of the  $p$ -orbital with equal facility, leading to a racemic mixture of products.



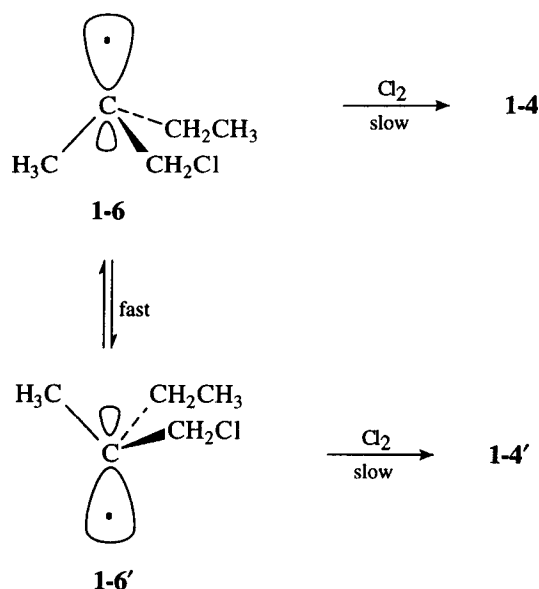
This result tells us that the stereochemical history of the chiral center is lost when a free radical is formed at that center. Therefore, if you want to form just a single enantiomer during substitution at a chiral center, a free-radical mechanism is not a good reaction to use.

**EXAMPLE 1-4** Suppose we knew from spectroscopic evidence (I.7-2) that free radicals prefer *non*-planar conformations such as **1-6**. How could we still account for the observed racemization?



1-6

**Solution** The racemization could still be explained by theorizing that **1-6** undergoes reversible inversion (Problem I.8-13) to **1-6'** much faster than either radical reacts with chlorine:



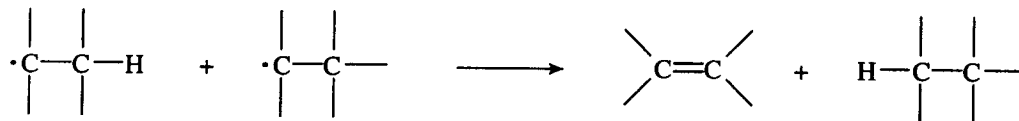
This type of rapid inversion is observed with amines and carbanions (Section 2-9).

While most radicals, especially those that are resonance stabilized, are essentially planar at the radical center, in some cases they are forced to adopt a non-planar structure (see Problem 1-3).

## 1-4. Pyrolysis and Cracking

Any molecule, when subjected to high enough temperature, will begin to fragment when the available thermal energy becomes comparable to the bond dissociation energies (I.9-1) in the molecule. This thermal fragmentation is called **pyrolysis**. When carrying out a pyrolysis, the reacting substance (or **starting material**, as it is usually called) is normally in the vapor phase. Furthermore, it is necessary to exclude other substances (e.g., oxygen) to prevent unwanted side reactions such as combustion (see Section 1-5).

Pyrolysis normally involves homolytic cleavage (I.4-2) of the weakest bond(s) in the molecule. This is sometimes described as **thermolysis** of the bond. The relatively high concentration of radicals formed during pyrolysis can lead to many different reactions of the types described in Section 1-3. For example, two radicals can collide and undergo disproportionation by hydrogen atom transfer, leading to two new product molecules:



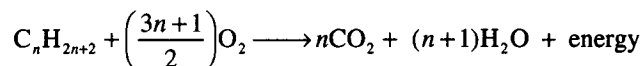
Unfortunately, with such high thermal energies available, the intermediate radicals are not very selective, so they tend to undergo many different fragmentation, rearrangement, recombination, and disproportionation processes, leading to many different products. However, certain molecules have structures that are predisposed to undergo specific thermal rearrangements, usually by pericyclic mechanisms (I.10-8). And other molecules, such as benzene (I.4-8) and other aromatic compounds, are exceptionally stable even at these high temperatures (in the absence of oxygen!).

It is often possible to find a substance that will catalyze (I.9-5) certain of the pyrolytic processes at lower temperatures, thereby favoring formation of fewer different products. This is the essence of **cracking**, the pyrolytic process by which crude petroleum (consisting of a horrendously complex mixture of molecules, most with high molecular weights) is converted to volatile hydrocarbons for use as fuels. The catalyst can change the mechanism of the reaction from homolytic cleavages to heterolytic cleavage involving carbocations (Section 2-5). However, although pyrolysis has a very important place in industrial-scale organic chemistry, it is of limited applicability in the laboratory.

## 1-5. Combustion and Its Consequences

Although alkanes as a class are quite unreactive compounds, they undergo one reaction that literally drives the world economy. That reaction is **combustion**, the thermal reaction with oxygen to give carbon dioxide, water (vapor), and *energy*. It is this reaction that powers our cars, airplanes, most of our electric generators, heats our homes, and in a direct way makes possible our high standard of living. The people of the United States use over 700 million gallons of crude petroleum *per day*, and we burn over 90% of it!

The general equation for the combustion of an alkane is



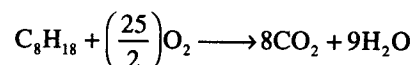
The energy released by this reaction can be measured calorimetrically, or estimated from bond strengths or other thermodynamic data (I.9-1). Because the C=O and H–O bonds are so strong (i.e., CO<sub>2</sub> and H<sub>2</sub>O are so stable), combustion is one of the most exothermic reactions known. In some cases we use the heat energy itself (to heat our homes, or to boil water to drive turbines), while in other applications (such as internal combustion engines) we extract mechanical energy from the expansion of the hot gaseous products.

The mechanism of combustion, like that of pyrolysis, is extremely complex and not fully understood. There is no question, however, that a variety of high-energy intermediates such as free radicals are involved.

**EXAMPLE 1-5** (a) What is the balanced equation for combustion of octane? (b) Given the bond dissociation energies ( $\Delta H_d$ , kJ/mol) below, estimate  $\Delta H$  for the combustion of gaseous octane, in kJ/g: C–C, 368; C–H, 410; O–O (in O<sub>2</sub>), 494; C=O, 803; H–O, 463.

### Solution

(a) From I.5-1 we know that octane is C<sub>8</sub>H<sub>18</sub>. Thus, substituting  $n = 8$  in the general equation for combustion, we arrive at this result:



(b) An octane molecule consists of 7 C–C bonds and 18 C–H bonds, and the oxygen has 12.5 O–O bonds. The products consist of 16 C=O bonds and 18 O–H bonds. Using Eq. (I.9-1), the heat of combustion per mole is given by

$$\begin{aligned}\Delta H &= \sum \Delta H_{d(\text{reactants})} - \sum \Delta H_{d(\text{products})} \\ &= 7(368) + 18(410) + 12.5(494) - [16(803) + 18(463)] \\ &= -5051 \text{ kJ/mol}\end{aligned}$$

Since the molecular weight (I.2-2) of octane is  $8(12) + 18(1) = 114$  g/mol, the heat of combustion *per gram* is

$$\Delta H = (-5051 \text{ kJ/mol}) / (114 \text{ g/mol}) = -44.3 \text{ kJ/g}$$

Recall (I.9-1) that the negative sign of  $\Delta H$  indicates an exothermic (heat-liberating) process.

There are several unfortunate consequences of the world's dependence on the combustion reaction as its main source of energy. First, the supply of fossil fuels (petroleum and coal) is finite and exhaustible. With our growing appetite for energy, it may only be two or three generations until they are simply gone, and with them our comfortable life-style. About 10% of our crude petroleum is diverted to petrochemical uses, providing starting materials for virtually all industrially important organic chemicals (see Chapter 11). Once the petroleum is gone, entire fields of technology will disappear.

Of course, it can be argued that the exhaustion of fossil fuels is not all bad. We now know that the products of combustion, mainly the carbon dioxide, are accumulating in our atmosphere. Unfortunately, the tropical rain forests, which photochemically convert this CO<sub>2</sub> back to oxygen, are being decimated each year to make room for the burgeoning human population. The ever-

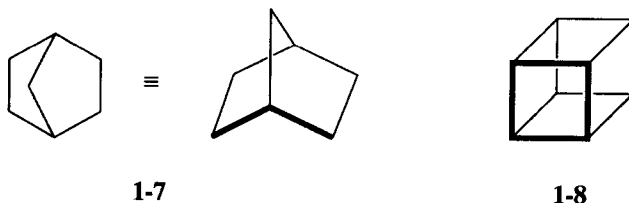
increasing concentration of  $\text{CO}_2$  causes the atmosphere to absorb more and more solar radiation, which leads to a gradual warming known as the **greenhouse effect**. The ultimate result of this warming may be significant changes in weather patterns, ability to grow crops, and perhaps even life as we know it.

In the final analysis, there is only one essentially limitless and clean energy source, and that is the sun. Until we can learn to harvest its output efficiently, we will continue to move closer to a precipice unprecedented in human history. The sooner we can reduce our dependence on petroleum fuels, the more time we will have to develop alternate technologies based on solar energy and renewable resources (such as cellulose from plants) as chemical feedstocks.

## 1-6. Cycloalkanes with Small Rings

Cycloalkanes having rings with at least five members exhibit relatively little ring strain (the total of angle strain and eclipsing strain; I.7-3,4), so they behave pretty much like their acyclic alkane cousins. However, molecules with three- or four-membered rings are much more reactive, a direct consequence of 110–115 kJ/mol of ring strain (Example I.7-11). Furthermore, the higher  $p$ -orbital character (I.3-6) of the C–C bonds in such compounds often makes them behave like unsaturated compounds with  $\pi$ -bonds. Thus, cyclopropane undergoes some of the same addition reactions that typical alkenes do, as we shall discover in Chapter 3.

The effect of ring strain is cumulative with the number of small rings. For example, bicyclo[2.2.1]heptane 1-7 can be seen to have two five-membered rings that share three atoms. It is found to have 63 kJ/mol of strain. And cubane, 1-8, a perfect cube of four-membered rings, has 656 kJ/mol of strain!



## SUMMARY

1. As a class, saturated hydrocarbons (alkanes and cycloalkanes) are relatively unreactive compounds because they are composed of strong, non-polar C–C and C–H bonds. They are also essentially non-acidic and non-basic. This makes saturated hydrocarbons very useful as inert solvents in a variety of applications.
2. The only exceptions to the above generalization are cycloalkanes with small (three- or four-membered), strained rings; such compounds bear a resemblance to alkenes in their reactivity.
3. The few reactions that saturated hydrocarbons *do* undergo include free-radical substitution, combustion, and pyrolytic cracking. Of these, the latter two are extremely important from the standpoint of world economics and industry. However, only the free-radical substitution reaction is useful in the laboratory.
4. Free-radical substitution at a chiral center involves racemization at that center, indicating that free-radical intermediates are either planar ( $sp^2$ -hybridized) or rapidly inverting.
5. The people of the world must in the near future develop energy sources other than fossil fuels if our quality of life is to be preserved.

## SUMMARY OF REACTIONS

Name <sup>a</sup>	Net reaction	Mechanism
R.1-1*: Halogenation (free-radical substitution)	$\text{R}-\text{H} \xrightarrow[\text{In}\cdot]{\text{X}_2} \text{R}-\text{X} \quad (\text{X} = \text{Cl}, \text{Br})$	Radical chain
R.1-2: Combustion	$\text{C}_n\text{H}_{2n+2} + \left(\frac{3n+1}{2}\right)\text{O}_2 \longrightarrow n\text{CO}_2 + (n+1)\text{H}_2\text{O}$	Complex

<sup>a</sup>An asterisk (\*) indicates that stereoisomers can be formed.



## RAISE YOUR GRADES

Can you define these new terms...?

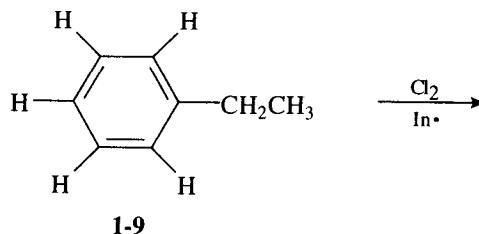
- |   |   |
|---|---|
| <input checked="" type="checkbox"/> aliphatic         | <input checked="" type="checkbox"/> dimer       |
| <input checked="" type="checkbox"/> pyrolysis         | <input checked="" type="checkbox"/> thermolysis |
| <input checked="" type="checkbox"/> cracking          | <input checked="" type="checkbox"/> combustion  |
| <input checked="" type="checkbox"/> greenhouse effect | <input checked="" type="checkbox"/> ring strain |

Can you explain...?

- ☒ why saturated hydrocarbons are relatively non-reactive under most conditions
- ☒ why many saturated hydrocarbons are useful as solvents
- ☒ the types of reactions that saturated hydrocarbons *do* undergo
- ☒ why free-radical substitution leads to racemization at the reaction center
- ☒ why small-ring cycloalkanes exhibit higher reactivity than other saturated hydrocarbons
- ☒ why we need to develop energy sources other than fossil fuels

## SOLVED PROBLEMS

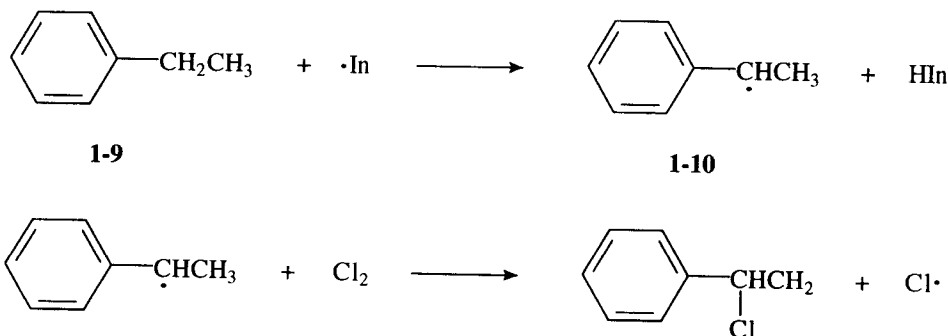
**PROBLEM 1-1** (a) Predict the major product from the reaction below, and suggest a mechanism for its formation.



(b) How might you determine the stereochemistry of free-radical substitution at a non-chiral center, e.g., the  $\text{CH}_2$  group in **1-9**?

### Solution

- (a) There are three “types” of hydrogens in this molecule: primary ( $\text{CH}_3$ ), secondary ( $\text{CH}_2$ ), and aromatic. The aromatic hydrogens, by virtue of being attached to  $sp^2$ -hybridized carbons, are the most strongly bonded, and hence the least readily abstracted. In fact, for all intents and purposes, only hydrogens attached to  $sp^3$ -hybridized carbons undergo free-radical substitution. We would therefore predict that the  $\text{CH}_2$  hydrogens are the most readily abstracted. Furthermore, the **benzyl radical 1-10** thereby produced would be resonance stabilized, as was **1-1**.



- (b) A  $\text{CH}_2$  group is achiral, so the stereochemistry (i.e., racemization, inversion, etc.) of substitution cannot be directly determined. What we need is a way to make it chiral, without disturbing