ORGANIC CHEMISTRY

FRANCIS A. CAREY

Department of Chemistry
University of Virginia

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ABOUT THE COVER

The cover depicts a new kind of molecular structure, one characterized by a spherical cluster of 60 carbon atoms. This compound, referred to as "buckminsterfullerene," has been described by Professor Richard E. Smalley and his coworkers in the Chemistry Department at Rice University. They suggest that it may be present among the products formed by high-vacuum laser vaporization of graphite. The interior of the molecule is large enough to accommodate other atoms and the + sign represents an atom of lanthanum trapped within the spherical cavity. The colored dots indicate the approximate van der Waals surface of the molecule. Theoretical calculations indicate that buckminsterfullerene and its metal complexes should be quite stable, yet further research is needed to conclusively establish the proposed structure.

In addition to Professor Smalley, I would also like to thank Professor Florante Quiocho and John C. Spurlino of the Biochemistry Department at Rice for permission to reproduce their computer graphics depiction of buckminsterfullerene.

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INTRODUCTION TO FUNCTIONAL GROUPS. ALCOHOLS AND ALKYL HALIDES

CHAPTER 4

This chapter introduces the principles of chemical reactions of organic compounds. A particularly important category of organic reactions is concerned with the interconversion of *functional groups.* A functional group is an atom or group of atoms in a molecule that experiences chemical change under a prescribed set of reaction conditions. An example of a functional group is the hydroxyl group (OH). On treatment with hydrogen halides, alcohols—substances that have a hydroxyl group bonded to sp^3 hybridized carbon—are transformed into alkyl halides.

$$\underset{\text{Alcohol}}{R{-}OH} + \underset{\text{Hydrogen halide}}{HX} \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Water}}{H_2O}$$

In this general equation the symbol R designates an alkyl group, ROH is an alcohol, and RX is an alkyl halide. During the reaction the functional group OH is replaced by the functional group X, but the remainder of the molecule (R) is unchanged.

The most important of the functional groups in organic chemistry are listed in the table on the inside front cover of this text. All of them will be discussed in detail in subsequent chapters.

Even a hydrogen substituent in an alkane can be a functional group. Alkanes react with halogens to form alkyl halides. The alkane is said to undergo *halogenation.*

$$\underset{\text{Alkane}}{R{-}H} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Hydrogen halide}}{HX}$$

Both the conversion of alcohols to alkyl halides and the halogenation of alkanes will be described in this chapter, with emphasis on their applications to chemical synthesis and their *mechanism.* The mechanism of a chemical reaction is a precise description, in as much detail as experimental data permit, of the path traveled by starting materials as they are converted to the products. In this chapter you will see how the mechanisms by which alcohols and alkanes are converted to alkyl halides are strikingly different from each other.

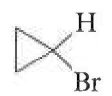
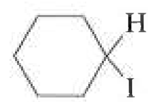
4.1 NOMENCLATURE OF ALCOHOLS AND ALKYL HALIDES

Several alcohols are commonplace substances, well known by familiar names that reflect their origin (wood alcohol, grain alcohol) or use (rubbing alcohol). The common name of wood alcohol is *methyl alcohol;* grain alcohol is *ethyl alcohol* and rubbing alcohol is *isopropyl alcohol.*

CH_3OH	CH_3CH_2OH	$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$
Methyl alcohol	Ethyl alcohol	Isopropyl alcohol

The common names of alcohols are derived by naming the alkyl group to which the hydroxyl group is attached, then adding the separate word *alcohol.*

Alkyl halides are named in a similar way. After specifying the alkyl group, the halide is identified in a separate word as *fluoride, chloride, bromide,* or *iodide,* as appropriate.

$CH_3CH_2CH_2F$	$(CH_3)_3CCH_2Cl$		
n-Propyl fluoride	Neopentyl chloride	Cyclopropyl bromide	Cyclohexyl iodide

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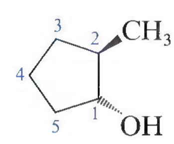
PROBLEM 4.1 Write structural formulas and give the common names of all the isomeric alkyl chlorides that have the molecular formula C_4H_9Cl.

Alcohols are given systematic IUPAC names by replacing the *-e* ending of the corresponding alkane name by *-ol*. The position of the hydroxyl group is indicated by number, choosing the sequence that assigns the lower locant to the carbon that bears the hydroxyl group.

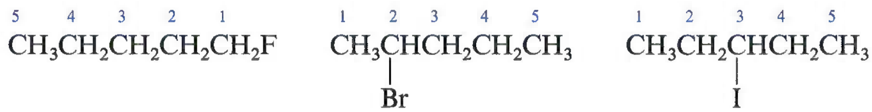
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH$	$\overset{1}{C}H_3\underset{\displaystyle OH}{\underset{|}{\overset{2}{C}}}H\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$	$\overset{1}{C}H_3\overset{2}{C}H_2\underset{\displaystyle OH}{\underset{|}{\overset{3}{C}}}H\overset{4}{C}H_2\overset{5}{C}H_3$
1-Propanol	2-Pentanol	3-Pentanol

Hydroxyl groups take precedence over alkyl groups in determining the direction in which a carbon chain is numbered.

$\overset{7}{C}H_3\underset{\displaystyle CH_3}{\underset{|}{\overset{6}{C}}}H\overset{5}{C}H_2\overset{4}{C}H_2\underset{\displaystyle OH}{\underset{|}{\overset{3}{C}}}H\overset{2}{C}H_2\overset{1}{C}H_3$	
6-Methyl-3-heptanol (not 2-methyl-5-heptanol)	*trans*-2-Methylcyclopentanol

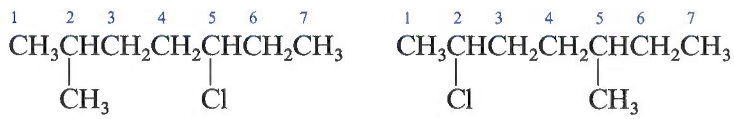
PROBLEM 4.2 Give systematic IUPAC names to all the isomeric $C_4H_{10}O$ alcohols.

Systematic nomenclature of alkyl halides treats the halogen as a substituent on an alkane chain. The carbon chain is numbered in the direction that gives the carbon bearing the halo- substituent the lower locant.



1-Fluoropentane 2-Bromopentane 3-Iodopentane

When the carbon chain bears both a halogen and an alkyl substituent, the two substituents are considered of equal rank and the chain is numbered so as to give the lower number to the substituent nearer the end of the chain.



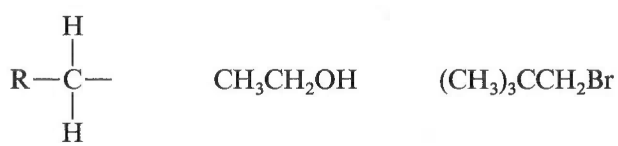
5-Chloro-2-methylheptane 2-Chloro-5-methylheptane

PROBLEM 4.3 Give the systematic names for all the isomeric alkyl chlorides having the molecular formula C_4H_9Cl.

Hydroxyl groups have precedence over halogen substituents in determining the direction of numbering. $FCH_2CH_2CH_2OH$, for example, is 3-fluoro-1-propanol, not 1-fluoro-3-propanol.

4.2 CLASSES OF ALCOHOLS AND ALKYL HALIDES

Alcohols and alkyl halides are classified as primary, secondary, or tertiary according to the classification of the carbon that bears the functional group (Section 2.10). In *primary alcohols* and *primary alkyl halides* the functional group is bonded to a primary carbon, that is, a carbon that bears one carbon substituent and two hydrogens.



Primary alkyl group; Ethyl alcohol (a primary alcohol); Neopentyl bromide (a primary alkyl halide)

In *secondary alcohols* and *secondary alkyl halides* the functional group is bonded to a secondary carbon atom; a secondary carbon is bonded to two other carbons and one hydrogen.

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