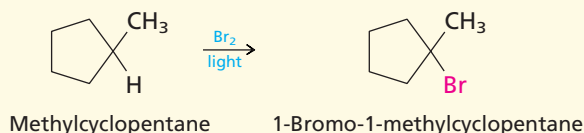


PROBLEM 4.18 Give the structure of the principal organic product formed by free-radical bromination of each of the following:

- (a) Methylcyclopentane (c) 2,2,4-Trimethylpentane
 (b) 1-Isopropyl-1-methylcyclopentane

SAMPLE SOLUTION (a) Write the structure of the starting hydrocarbon, and identify any tertiary hydrogens that are present. The only tertiary hydrogen in methylcyclopentane is the one attached to C-1. This is the one replaced by bromine.



This difference in selectivity between chlorination and bromination of alkanes needs to be kept in mind when one wishes to prepare an alkyl halide from an alkane:

1. Because chlorination of an alkane yields every possible monochloride, it is used only when all the hydrogens in an alkane are equivalent.
2. Bromination is normally used only to prepare tertiary alkyl bromides from alkanes.

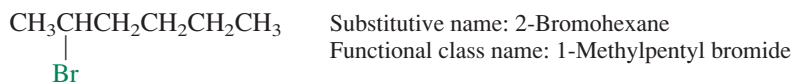
Selectivity is not an issue in the conversion of alcohols to alkyl halides. Except for certain limitations to be discussed in Section 8.15, the location of the halogen substituent in the product corresponds to that of the hydroxyl group in the starting alcohol.

4.19 SUMMARY

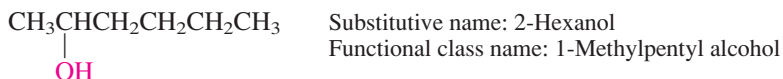
Chemical reactivity and functional group transformations involving the preparation of alkyl halides from alcohols and from alkanes are the main themes of this chapter. Although the conversions of an alcohol or an alkane to an alkyl halide are both classified as substitutions, they proceed by very different mechanisms.

Section 4.1 **Functional groups** are the structural units responsible for the characteristic reactions of a molecule. The hydrocarbon chain to which a functional group is attached can often be considered as simply a supporting framework. The most common functional groups characterize the families of organic compounds listed on the inside front cover of the text.

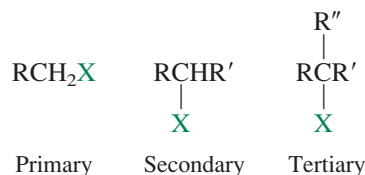
Section 4.2 Alcohols and alkyl halides may be named using either **substitutive** or **functional class** IUPAC nomenclature. In substitutive nomenclature alkyl halides are named as halogen derivatives of alkanes. The parent is the longest continuous chain that bears the halogen substituent, and in the absence of other substituents the chain is numbered from the direction that gives the lowest number to the carbon that bears the halogen. The functional class names of alkyl halides begin with the name of the alkyl group and end with the halide as a separate word.



Section 4.3 The substitutive names of alcohols are derived by replacing the *-e* ending of an alkane with *-ol*. The longest chain containing the OH group becomes the basis for the name. Functional class names of alcohols begin with the name of the alkyl group and end in the word *alcohol*.

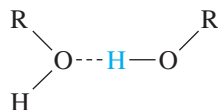


Section 4.4 Alcohols ($\text{X} = \text{OH}$) and alkyl halides ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$) are classified as primary, secondary, or tertiary according to the degree of substitution at the carbon that bears the functional group.



Section 4.5 The halogens (especially fluorine and chlorine) and oxygen are more electronegative than carbon, and the carbon–halogen bond in alkyl halides and the carbon–oxygen bond in alcohols are polar. Carbon is the positive end of the dipole and halogen or oxygen the negative end.

Section 4.6 Dipole/induced-dipole and dipole–dipole attractive forces make alcohols higher boiling than alkanes of similar molecular weight. The attractive force between —OH groups is called **hydrogen bonding**.



Hydrogen bonding between the hydroxyl group of an alcohol and water makes the water-solubility of alcohols greater than that of hydrocarbons. Low-molecular-weight alcohols [CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, and $(\text{CH}_3)_2\text{CHOH}$] are soluble in water in all proportions. Alkyl halides are insoluble in water.

Section 4.7 See Table 4.4

Section 4.8 Secondary and tertiary alcohols react with hydrogen halides by a mechanism that involves formation of a carbocation intermediate in the rate-determining step.

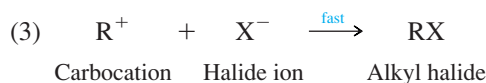
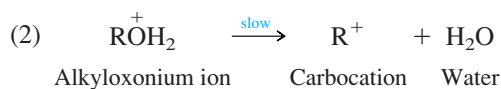
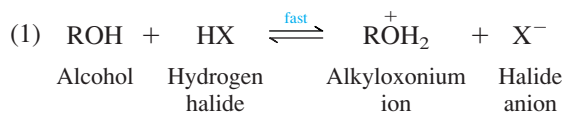
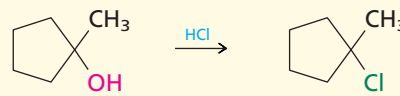
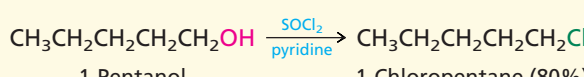
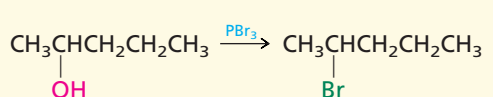
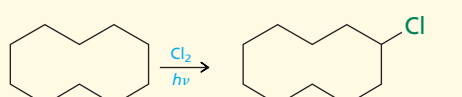
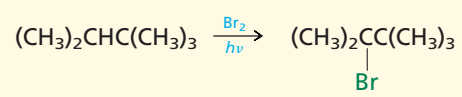


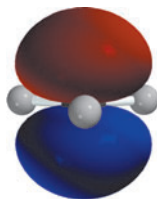
TABLE 4.4 Conversions of Alcohols and Alkanes to Alkyl Halides

Reaction (section) and comments	General equation and specific example(s)
Reactions of alcohols with hydrogen halides (Section 4.7) Alcohols react with hydrogen halides to yield alkyl halides. The reaction is useful as a synthesis of alkyl halides. The reactivity of hydrogen halides decreases in the order $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Alcohol reactivity decreases in the order tertiary > secondary > primary > methyl.	$\text{ROH} + \text{HX} \longrightarrow \text{RX} + \text{H}_2\text{O}$ <p>Alcohol Hydrogen halide Alkyl halide Water</p>  <p>1-Methylcyclopentanol 1-Chloro-1-methylcyclopentane (96%)</p>
Reaction of alcohols with thionyl chloride (Section 4.13) Thionyl chloride is a synthetic reagent used to convert alcohols to alkyl chlorides.	$\text{ROH} + \text{SOCl}_2 \longrightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$ <p>Alcohol Thionyl chloride Alkyl chloride Sulfur dioxide Hydrogen chloride</p>  <p>1-Pentanol 1-Chloropentane (80%)</p>
Reaction of alcohols with phosphorus tribromide (Section 4.13) As an alternative to converting alcohols to alkyl bromides with hydrogen bromide, the inorganic reagent phosphorus tribromide is sometimes used.	$3\text{ROH} + \text{PBr}_3 \longrightarrow 3\text{RBr} + \text{H}_3\text{PO}_3$ <p>Alcohol Phosphorus tribromide Alkyl bromide Phosphorous acid</p>  <p>2-Pentanol 2-Bromopentane (67%)</p>
Free-radical halogenation of alkanes (Sections 4.14 through 4.18) Alkanes react with halogens by substitution of a halogen for a hydrogen on the alkane. The reactivity of the halogens decreases in the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. The ease of replacing a hydrogen decreases in the order tertiary > secondary > primary > methyl. Chlorination is not very selective and so is used only when all the hydrogens of the alkane are equivalent. Bromination is highly selective, replacing tertiary hydrogens much more readily than secondary or primary ones.	$\text{RH} + \text{X}_2 \longrightarrow \text{RX} + \text{HX}$ <p>Alkane Halogen Alkyl halide Hydrogen halide</p>  <p>Cyclodecane Cyclodecyl chloride (64%)</p>  <p>2,2,3-Trimethylbutane 2-Bromo-2,3,3-trimethylbutane (80%)</p>

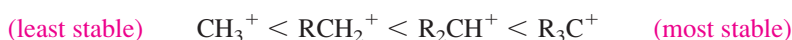
Section 4.9

The potential energy diagrams for separate elementary steps can be merged into a diagram for the overall process. The diagram for the reaction of a secondary or tertiary alcohol with a hydrogen halide is characterized by two intermediates and three transition states. The reaction is classified as a unimolecular **nucleophilic substitution**, abbreviated as $\text{S}_{\text{N}}1$.

Section 4.10 Carbocations contain a positively charged carbon with only three atoms or groups attached to it. This carbon is sp^2 -hybridized and has a vacant $2p$ orbital.



Carbocations are stabilized by alkyl substituents attached directly to the positively charged carbon. Alkyl groups are *electron-releasing* substituents. Stability increases in the order:



Carbocations are strongly **electrophilic** (Lewis acids) and react with **nucleophiles** (Lewis bases).

Section 4.11 The rate at which alcohols are converted to alkyl halides depends on the rate of carbocation formation: tertiary alcohols are most reactive; primary alcohols and methanol are least reactive.

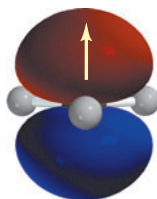
Section 4.12 Primary alcohols do not react with hydrogen halides by way of carbocation intermediates. The nucleophilic species (Br^- for example) attacks the alkyloxonium ion and “pushes off” a water molecule from carbon in a bimolecular step. This step is rate-determining, and the mechanism is $\text{S}_{\text{N}}2$.

Section 4.13 See Table 4.4

Section 4.14 See Table 4.4

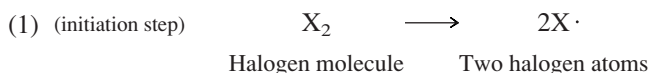
Section 4.15 Methane reacts with Cl_2 to give chloromethane, dichloromethane, trichloromethane, and tetrachloromethane.

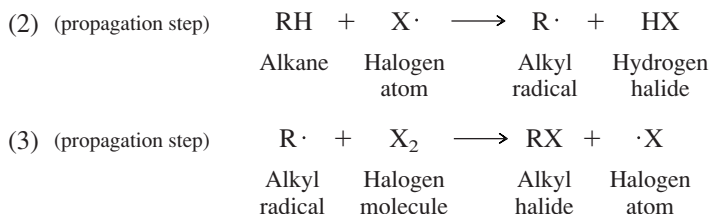
Section 4.16 Chlorination of methane, and halogenation of alkanes generally, proceed by way of **free-radical** intermediates. Alkyl radicals are neutral and have an unpaired electron on carbon.



Like carbocations, free radicals are stabilized by alkyl substituents. The order of free-radical stability parallels that of carbocation stability.

Section 4.17 The elementary steps (1) through (3) describe a free-radical chain mechanism for the reaction of an alkane with a halogen.






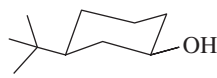
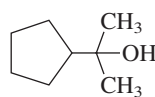
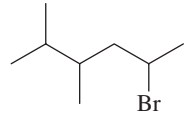
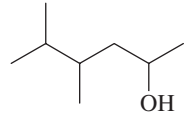
Section 4.18 See Table 4.4

PROBLEMS

4.19 Write structural formulas for each of the following alcohols and alkyl halides:

- | | |
|--|--|
| (a) Cyclobutanol
(b) <i>sec</i> -Butyl alcohol
(c) 3-Heptanol
(d) <i>trans</i> -2-Chlorocyclopentanol | (e) 2,6-Dichloro-4-methyl-4-octanol
(f) <i>trans</i> -4- <i>tert</i> -Butylcyclohexanol
(g) 1-Cyclopropylethanol
(h) 2-Cyclopropylethanol |
|--|--|

4.20 Name each of the following compounds according to substitutive IUPAC nomenclature:

- | | |
|--|---|
| (a) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Br}$
(b) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$
(c) $\text{Cl}_3\text{CCH}_2\text{Br}$
(d) Cl_2CHCHBr
<div style="text-align: center; margin-left: 40px;">  </div> (e) $\text{CF}_3\text{CH}_2\text{OH}$
(f)  | (g) 
(h) 
(i)  |
|--|---|

4.21 Handbooks are notorious for listing compounds according to their common names. One gives the name “*sec*-isoamyl alcohol” for a compound which could be called 1,2-dimethylpropyl alcohol according to the IUPAC functional class rules. The best name for this compound is the substitutive IUPAC name. What is it?



4.22 Write structural formulas, or build molecular models for all the constitutionally isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$. Assign a substitutive and a functional class name to each one, and specify whether it is a primary, secondary, or tertiary alcohol.



4.23 A hydroxyl group is a somewhat “smaller” substituent on a six-membered ring than is a methyl group. That is, the preference of a hydroxyl group for the equatorial orientation is less pronounced than that of a methyl group. Given this information, write structural formulas or build molecular models for all the isomeric methylcyclohexanols, showing each one in its most stable conformation. Give the substitutive IUPAC name for each isomer.

4.24 By assuming that the heat of combustion of the *cis* isomer was larger than the *trans*, structural assignments were made many years ago for the stereoisomeric 2-, 3-, and 4-methylcyclohexanols. This assumption is valid for two of the stereoisomeric pairs but is incorrect for the other. For which pair of stereoisomers is the assumption incorrect? Why?