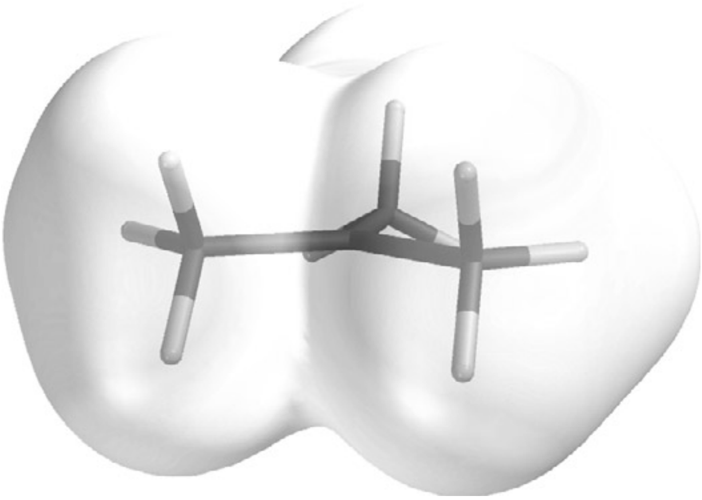
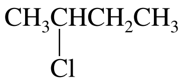
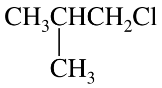
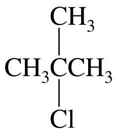


CHAPTER 4

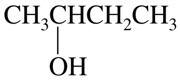
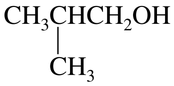
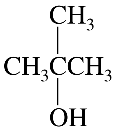
ALCOHOLS AND ALKYL HALIDES

SOLUTIONS TO TEXT PROBLEMS

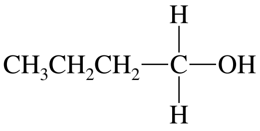
4.1 There are four C_4H_9 alkyl groups, and so there are four C_4H_9Cl alkyl chlorides. Each may be named by both the functional class and substitutive methods. The functional class name uses the name of the alkyl group followed by the halide as a second word. The substitutive name modifies the name of the corresponding alkane to show the location of the halogen atom.

	Functional class name	**Substitutive name**
$CH_3CH_2CH_2CH_2Cl$	*n*-Butyl chloride (Butyl chloride)	1-Chlorobutane
 $CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}HCH_2CH_3$	*sec*-Butyl chloride (1-Methylpropyl chloride)	2-Chlorobutane
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2Cl$	Isobutyl chloride (2-Methylpropyl chloride)	1-Chloro-2-methylpropane
 $CH_3\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle Cl}{\underset{\vert}{C}}}}CH_3$	*tert*-Butyl chloride (1,1-Dimethylethyl chloride)	2-Chloro-2-methylpropane

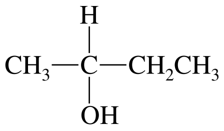
4.2 Alcohols may also be named using both the functional class and substitutive methods, as in the previous problem.

	Functional class name	Substitutive name
$CH_3CH_2CH_2CH_2OH$	*n*-Butyl alcohol (Butyl alcohol)	1-Butanol
 $CH_3\underset{\substack{\mid\\ OH}}{C}HCH_2CH_3$	*sec*-Butyl alcohol (1-Methylpropyl alcohol)	2-Butanol
 $CH_3\underset{\substack{\mid\\ CH_3}}{C}HCH_2OH$	Isobutyl alcohol (2-Methylpropyl alcohol)	2-Methyl-1-propanol
 $CH_3\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ OH}}{C}}CH_3$	*tert*-Butyl alcohol (1,1-Dimethylethyl alcohol)	2-Methyl-2-propanol

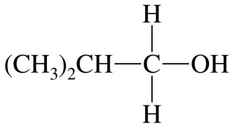
4.3 Alcohols are classified as primary, secondary, or tertiary according to the number of carbon substituents attached to the carbon that bears the hydroxyl group.



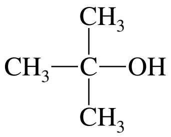
Primary alcohol
(one alkyl group bonded to —CH_2OH)



Secondary alcohol
(two alkyl groups bonded to >CHOH)

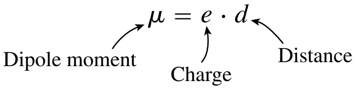


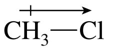
Primary alcohol
(one alkyl group bonded to —CH_2OH)



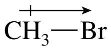
Tertiary alcohol
(three alkyl groups bonded to >COH)

4.4 Dipole moment is the product of charge and distance. Although the electron distribution in the carbon–chlorine bond is more polarized than that in the carbon–bromine bond, this effect is counterbalanced by the longer carbon–bromine bond distance.


$$\mu = e \cdot d$$

 $\overset{+\!\!\longrightarrow}{CH_3—Cl}$

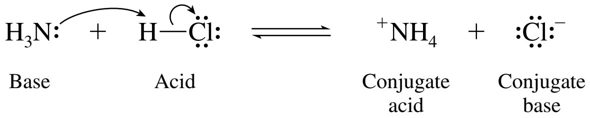
Methyl chloride
(greater value of *e*)
μ 1.9 D

 $\overset{+\!\!\longrightarrow}{CH_3—Br}$

Methyl bromide
(greater value of *d*)
μ 1.8 D

4.5 All the hydrogens in dimethyl ether (CH_3OCH_3) are bonded to carbon; therefore, intermolecular hydrogen bonding between dimethyl ether molecules does not take place, and its boiling point is lower than that of ethanol (CH_3CH_2OH), where hydrogen bonding involving the —OH group is important.

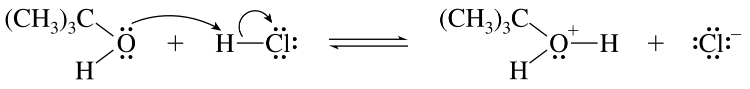
4.6 Ammonia is a base and abstracts (accepts) a proton from the acid (proton donor) hydrogen chloride.



4.7 Since the pK_a of HCN is given as 9.1, its $K_a = 10^{-9.1}$. In more conventional notation, $K_a = 8 \times 10^{-10}$. Hydrogen cyanide is a weak acid.

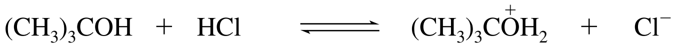
4.8 Hydrogen cyanide is a weak acid, but it is a stronger acid than water ($pK_a = 15.7$). Since HCN is a stronger acid than water, its conjugate base (CN^-) is a weaker base than hydroxide (HO^-), which is the conjugate base of water.

4.9 An unshared electron pair on oxygen abstracts the proton from hydrogen chloride.



Base Acid Conjugate acid Conjugate base

4.10 In any proton-transfer process, the position of equilibrium favors formation of the weaker acid and the weaker base from the stronger acid and base. Alkyloxonium ions (ROH_2^+) have approximately the same acidity as hydronium ion (H_3O^+, $pK_a = -1.7$). Thus hydrogen chloride ($pK_a \approx -7$) is the stronger acid. *tert*-Butyl alcohol is the stronger base because it is the conjugate of the weaker acid (*tert*-butyloxonium ion).

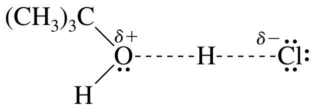


$$(CH_3)_3COH + HCl \rightleftharpoons (CH_3)_3C\overset{+}{O}H_2 + Cl^-$$

$(CH_3)_3COH$	HCl	$(CH_3)_3C\overset{+}{O}H_2$	Cl^-
Stronger base	($pK_a \approx -7$) Stronger acid	($pK_a \approx -1.7$) Weaker acid	Weaker base

The equilibrium constant for proton transfer from hydrogen chloride to *tert*-butyl alcohol is much greater than 1.

4.11 The proton being transferred is partially bonded to the oxygen of *tert*-butyl alcohol and to chloride at the transition state.



4.12 (*b*) Hydrogen chloride converts tertiary alcohols to tertiary alkyl chlorides.

$$(CH_3CH_2)_3COH + HCl \longrightarrow (CH_3CH_2)_3CCl + H_2O$$

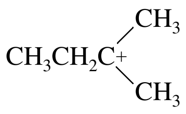
$(CH_3CH_2)_3COH$	HCl	$(CH_3CH_2)_3CCl$	H_2O
3-Ethyl-3-pentanol	Hydrogen chloride	3-Chloro-3-ethylpentane	Water

(*c*) 1-Tetradecanol is a primary alcohol having an unbranched 14-carbon chain. Hydrogen bromide reacts with primary alcohols to give the corresponding primary alkyl bromide.

$$CH_3(CH_2)_{12}CH_2OH + HBr \longrightarrow CH_3(CH_2)_{12}CH_2Br + H_2O$$

$CH_3(CH_2)_{12}CH_2OH$	HBr	$CH_3(CH_2)_{12}CH_2Br$	H_2O
1-Tetradecanol	Hydrogen bromide	1-Bromotetradecane	Water

4.13 The order of carbocation stability is tertiary > secondary > primary. There is only one $C_5H_{11}^+$ carbocation that is tertiary, and so that is the most stable one.

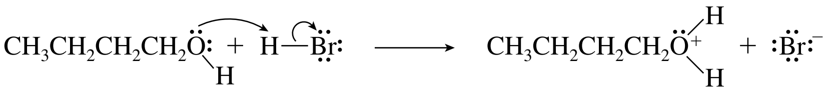


1,1-Dimethylpropyl cation

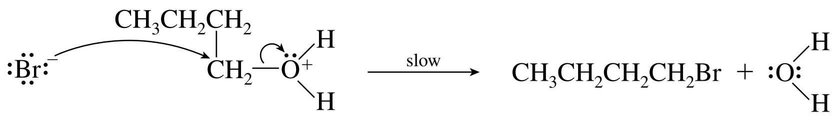
4.14 1-Butanol is a primary alcohol; 2-butanol is a secondary alcohol. A carbocation intermediate is possible in the reaction of 2-butanol with hydrogen bromide but not in the corresponding reaction of 1-butanol.

The mechanism of the reaction of 1-butanol with hydrogen bromide proceeds by displacement of water by bromide ion from the protonated form of the alcohol (the alkyloxonium ion).

Protonation of the alcohol:



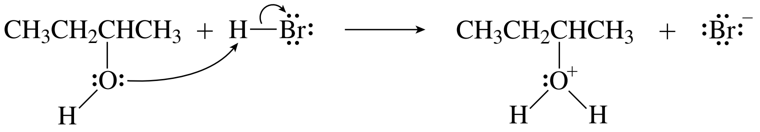
Displacement of water by bromide:



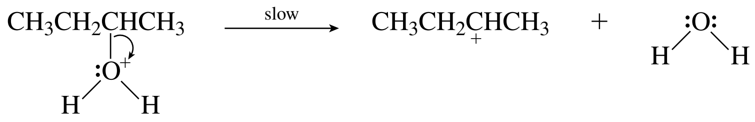
The slow step, displacement of water by bromide from the oxonium ion, is bimolecular. The reaction of 1-butanol with hydrogen bromide follows the S_N2 mechanism.

The reaction of 2-butanol with hydrogen bromide involves a carbocation intermediate.

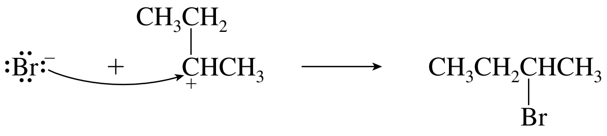
Protonation of the alcohol:



Dissociation of the oxonium ion:

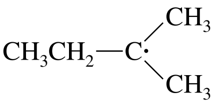


Capture of *sec*-butyl cation by bromide:

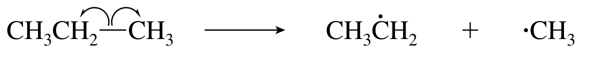


The slow step, dissociation of the oxonium ion, is unimolecular. The reaction of 2-butanol with hydrogen bromide follows the S_N1 mechanism.

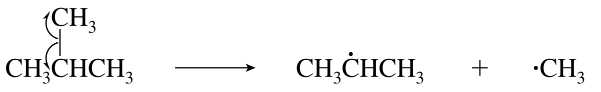
4.15 The most stable alkyl free radicals are tertiary. The tertiary free radical having the formula C_5H_{11} has the same skeleton as the carbocation in Problem 4.13.



4.16 (*b*) Writing the equations for carbon–carbon bond cleavage in propane and in 2-methylpropane, we see that a primary ethyl radical is produced by a cleavage of propane whereas a secondary isopropyl radical is produced by cleavage of 2-methylpropane.



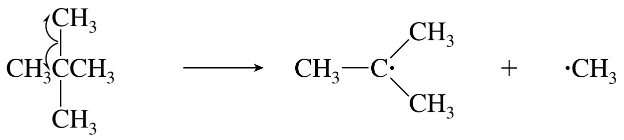
Propane Ethyl radical Methyl radical



2-Methylpropane Isopropyl radical Methyl radical

A secondary radical is more stable than a primary one, and so carbon–carbon bond cleavage of 2-methylpropane requires less energy than carbon–carbon bond cleavage of propane.

(*c*) Carbon–carbon bond cleavage of 2,2-dimethylpropane gives a tertiary radical.



2,2-Dimethylpropane *tert*-Butyl radical Methyl radical

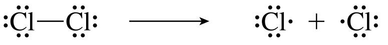
As noted in part (*b*), a secondary radical is produced on carbon–carbon bond cleavage of 2-methylpropane. We therefore expect a lower carbon–carbon bond dissociation energy for 2,2-dimethylpropane than for 2-methylpropane, since a tertiary radical is more stable than a secondary one.

4.17 First write the equation for the overall reaction.

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

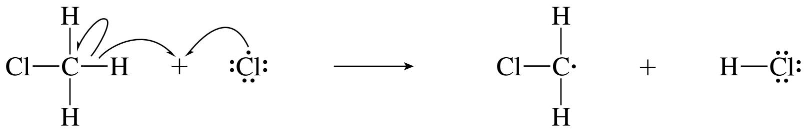
Chloromethane Chlorine Dichloromethane Hydrogen chloride

The initiation step is dissociation of chlorine to two chlorine atoms.



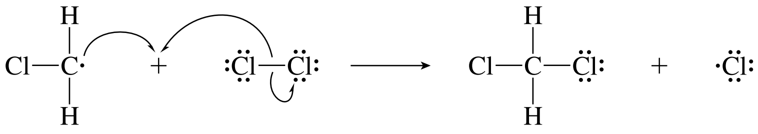
Chlorine 2 Chlorine atoms

A chlorine atom abstracts a hydrogen atom from chloromethane in the first propagation step.



Chloromethane Chlorine atom Chloromethyl radical Hydrogen chloride

Chloromethyl radical reacts with Cl_2 in the next propagation step.



Chloromethyl radical Chlorine Dichloromethane Chlorine atom

4.18 Writing the structural formula for ethyl chloride reveals that there are two nonequivalent sets of hydrogen atoms, in either of which a hydrogen is capable of being replaced by chlorine.

$$\mathrm{CH_3CH_2Cl} \xrightarrow[\text{light or heat}]{\mathrm{Cl_2}} \mathrm{CH_3CHCl_2} + \mathrm{ClCH_2CH_2Cl}$$

Ethyl chloride 1,1-Dichloroethane 1,2-Dichloroethane

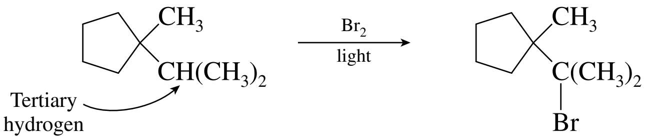
The two dichlorides are 1,1-dichloroethane and 1,2-dichloroethane.

4.19 Propane has six primary hydrogens and two secondary. In the chlorination of propane, the relative proportions of hydrogen atom removal are given by the product of the statistical distribution and the relative rate per hydrogen. Given that a secondary hydrogen is abstracted 3.9 times faster than a primary one, we write the expression for the amount of chlorination at the primary relative to that at the secondary position as:

$$\frac{\text{Number of primary hydrogens} \times \text{rate of abstraction of primary hydrogen}}{\text{Number of secondary hydrogens} \times \text{rate of abstraction of a secondary hydrogen}} = \frac{6 \times 1}{2 \times 3.9} = \frac{0.77}{1.00}$$

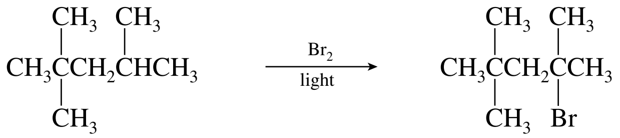
Thus, the percentage of propyl chloride formed is 0.77/1.77, or 43%, and that of isopropyl chloride is 57%. (The amounts actually observed are propyl 45%, isopropyl 55%.)

4.20 (*b*) In contrast with free-radical chlorination, alkane bromination is a highly selective process. The major organic product will be the alkyl bromide formed by substitution of a tertiary hydrogen with a bromine.



1-Isopropyl-1-methylcyclopentane 1-(1-Bromo-1-methylethyl)-1-methylcyclopentane

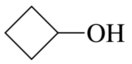
(*c*) As in part (*b*), bromination results in substitution of a tertiary hydrogen.



$$\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_3} \xrightarrow[\text{light}]{\mathrm{Br_2}} \mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{Br}}{\mathrm{C}}}\mathrm{CH_3}$$

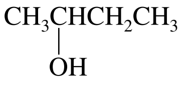
2,2,4-Trimethylpentane 2-Bromo-2,4,4-trimethylpentane

4.21 (*a*) Cyclobutanol has a hydroxyl group attached to a four-membered ring.



Cyclobutanol

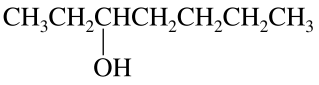
(*b*) *sec*-Butyl alcohol is the functional class name for 2-butanol.



$$\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH_3}$$

sec-Butyl alcohol

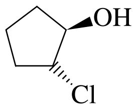
(*c*) The hydroxyl group is at C-3 of an unbranched seven-carbon chain in 3-heptanol.



$$\mathrm{CH_3CH_2}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH_2CH_2CH_3}$$

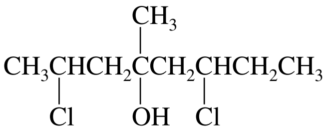
3-Heptanol

(*d*) A chlorine at C-2 is on the opposite side of the ring from the C-1 hydroxyl group in *trans*-2-chlorocyclopentanol. Note that it is not necessary to assign a number to the carbon that bears the hydroxyl group; naming the compound as a derivative of cyclopentanol automatically requires the hydroxyl group to be located at C-1.



trans-2-Chlorocyclopentanol

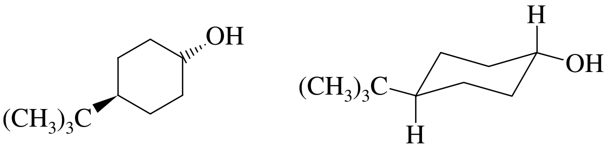
(*e*) This compound is an alcohol in which the longest continuous chain that incorporates the hydroxyl function has eight carbons. It bears chlorine substituents at C-2 and C-6 and methyl and hydroxyl groups at C-4.



$$\mathrm{CH_3\underset{Cl}{CH}CH_2\overset{CH_3}{\underset{OH}{C}}CH_2\underset{Cl}{CH}CH_2CH_3}$$

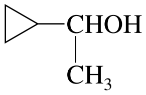
2,6-Dichloro-4-methyl-4-octanol

(*f*) The hydroxyl group is at C-1 in *trans*-4-*tert*-butylcyclohexanol; the *tert*-butyl group is at C-4. The structures of the compound can be represented as shown at the left; the structure at the right depicts it in its most stable conformation.



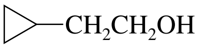
trans-4-*tert*-Butylcyclohexanol

(*g*) The cyclopropyl group is on the same carbon as the hydroxyl group in 1-cyclopropylethanol.



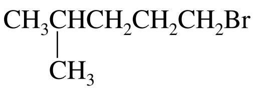
1-Cyclopropylethanol

(*h*) The cyclopropyl group and the hydroxyl group are on adjacent carbons in 2-cyclopropylethanol.



2-Cyclopropylethanol

4.22 (*a*) This compound has a five-carbon chain that bears a methyl substituent and a bromine. The numbering scheme that gives the lower number to the substituent closest to the end of the chain is chosen. Bromine is therefore at C-1, and methyl is a substituent at C-4.



$$\mathrm{CH_3\underset{CH_3}{CH}CH_2CH_2CH_2Br}$$

1-Bromo-4-methylpentane

(*b*) This compound has the same carbon skeleton as the compound in part (*a*) but bears a hydroxyl group in place of the bromine and so is named as a derivative of 1-pentanol.

$$\mathrm{CH_3\underset{\substack{|\\ \mathrm{CH_3}}}{C}HCH_2CH_2CH_2OH}$$

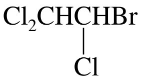
4-Methyl-1-pentanol

(*c*) This molecule is a derivative of ethane and bears three chlorines and one bromine. The name 2-bromo-1,1,1-trichloroethane gives a lower number at the first point of difference than 1-bromo-2,2,2-trichloroethane.

$$\mathrm{Cl_3CCH_2Br}$$

2-Bromo-1,1,1-trichloroethane

(*d*) This compound is a constitutional isomer of the preceding one. Regardless of which carbon the numbering begins at, the substitution pattern is 1,1,2,2. Alphabetical ranking of the halogens therefore dictates the direction of numbering. Begin with the carbon that bears bromine.



$$\mathrm{Cl_2CH\underset{\substack{|\\ \mathrm{Cl}}}{C}HBr}$$

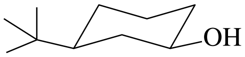
1-Bromo-1,2,2-trichloroethane

(*e*) This is a trifluoro derivative of ethanol. The direction of numbering is dictated by the hydroxyl group, which is at C-1 in ethanol.

$$\mathrm{CF_3CH_2OH}$$

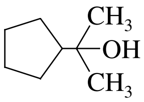
2,2,2-Trifluoroethanol

(*f*) Here the compound is named as a derivative of cyclohexanol, and so numbering begins at the carbon that bears the hydroxyl group.



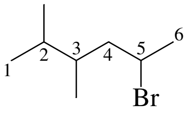
cis-3-*tert*-Butylcyclohexanol

(*g*) This alcohol has its hydroxyl group attached to C-2 of a three-carbon continuous chain; it is named as a derivative of 2-propanol.



2-Cyclopentyl-2-propanol

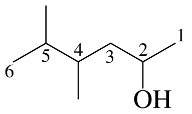
(*h*) The six carbons that form the longest continuous chain have substituents at C-2, C-3, and C-5 when numbering proceeds in the direction that gives the lowest locants to substituents at the first point of difference. The substituents are cited in alphabetical order.



5-Bromo-2,3-dimethylhexane

Had numbering begun in the opposite direction, the locants would be 2,4,5 rather than 2,3,5.

(*i*) Hydroxyl controls the numbering because the compound is named as an alcohol.

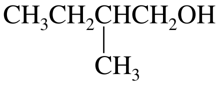


4,5-Dimethyl-2-hexanol

4.23 Primary alcohols are alcohols in which the hydroxyl group is attached to a carbon atom which has one alkyl substituent and two hydrogens. Four primary alcohols have the molecular formula $C_5H_{12}O$. The functional class name for each compound is given in parentheses.

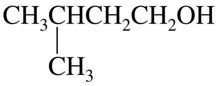
$CH_3CH_2CH_2CH_2CH_2OH$

1-Pentanol
(Pentyl alcohol)



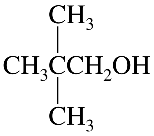
$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH$

2-Methyl-1-butanol
(2-Methylbutyl alcohol)



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH$

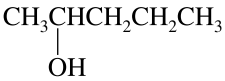
3-Methyl-1-butanol
(3-Methylbutyl alcohol)



$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2OH$

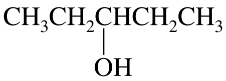
2,2-Dimethyl-1-propanol
(2,2-Dimethylpropyl alcohol)

Secondary alcohols are alcohols in which the hydroxyl group is attached to a carbon atom which has two alkyl substituents and one hydrogen. There are three secondary alcohols of molecular formula $C_5H_{12}O$:



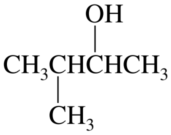
$CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3$

2-Pentanol
(1-Methylbutyl alcohol)



$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CH_3$

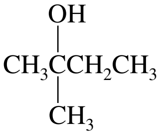
3-Pentanol
(1-Ethylpropyl alcohol)



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

3-Methyl-2-butanol
(1,2-Dimethylpropyl alcohol)

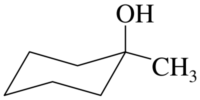
Only 2-methyl-2-butanol is a tertiary alcohol (three alkyl substituents on the hydroxyl-bearing carbon):



$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_3$

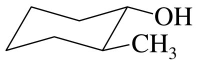
2-Methyl-2-butanol
(1,1-Dimethylpropyl alcohol)

4.24 The first methylcyclohexanol to be considered is 1-methylcyclohexanol. The preferred chair conformation will have the larger methyl group in an equatorial orientation, whereas the smaller hydroxyl group will be axial.

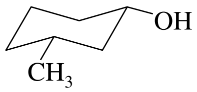


Most stable conformation of
1-methylcyclohexanol

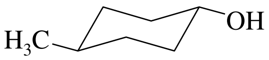
In the other isomers methyl and hydroxyl will be in a 1,2, 1,3, or 1,4 relationship and can be cis or trans in each. We can write the preferred conformation by recognizing that the methyl group will always be equatorial and the hydroxyl either equatorial or axial.



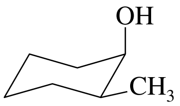
trans-2-Methylcyclohexanol



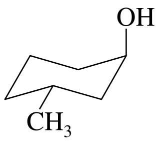
cis-3-Methylcyclohexanol



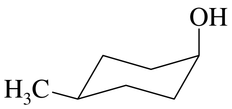
trans-4-Methylcyclohexanol



cis-2-Methylcyclohexanol

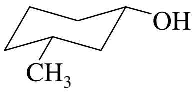


trans-3-Methylcyclohexanol

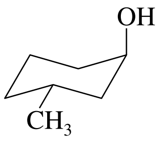


cis-4-Methylcyclohexanol

4.25 The assumption is incorrect for the 3-methylcyclohexanols. *cis*-3-Methylcyclohexanol is more stable than *trans*-3-methylcyclohexanol because the methyl group and the hydroxyl group are both equatorial in the cis isomer, whereas one substituent must be axial in the trans.

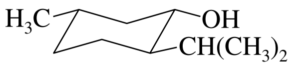


cis-3-Methylcyclohexanol more stable; *smaller* heat of combustion



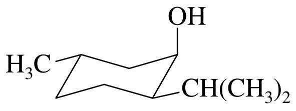
trans-3-Methylcyclohexanol less stable; *larger* heat of combustion

4.26 (*a*) The most stable conformation will be the one with all the substituents equatorial.



The hydroxyl group is trans to the isopropyl group and cis to the methyl group.

(*b*) All three substituents need not always be equatorial; instead, one or two of them may be axial. Since neomenthol is the second most stable stereoisomer, we choose the structure with *one* axial substituent. Furthermore, we choose the structure with the smallest substituent (the hydroxyl group) as the axial one. Neomenthol is shown as follows:



4.27 In all these reactions the negatively charged atom abstracts a proton from an acid.

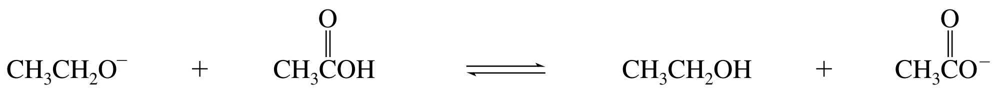
(*a*) $HI + HO^- \rightleftharpoons I^- + H_2O$

Hydrogen iodide: acid (stronger acid, $K_a \approx 10^{10}$)

Hydroxide ion: base

Iodide ion: conjugate base

Water: conjugate acid (weaker acid, $K_a \approx 10^{-16}$)


(*b*) $CH_3CH_2O^- + CH_3\overset{\displaystyle O}{\overset{\|}{C}}OH \rightleftharpoons CH_3CH_2OH + CH_3\overset{\displaystyle O}{\overset{\|}{C}}O^-$

Ethoxide ion: base

Acetic acid: acid (stronger acid, $K_a \approx 10^{-5}$)

Ethanol: conjugate acid (weaker acid, $K_a \approx 10^{-16}$)

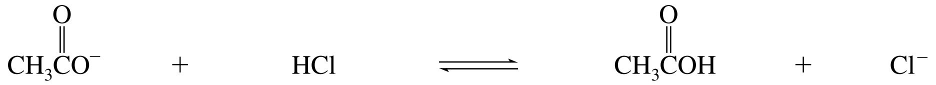
Acetate ion: conjugate base

(*c*)

$$\mathrm{HF} + \mathrm{H_2N^-} \rightleftharpoons \mathrm{F^-} + \mathrm{H_3N}$$

Hydrogen fluoride: acid (stronger acid, $K_a \approx 10^{-4}$)	Amide ion: base	Fluoride ion: conjugate base	Ammonia: conjugate acid (weaker acid, $K_a \approx 10^{-36}$)

(*d*)



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}O^-} + \mathrm{HCl} \rightleftharpoons \mathrm{CH_3\overset{O}{\overset{\|}{C}}OH} + \mathrm{Cl^-}$$

Acetate ion: base	Hydrogen chloride: acid (stronger acid, $K_a \approx 10^{7}$)	Acetic acid: conjugate acid (weaker acid, $K_a \approx 10^{-5}$)	Chloride ion: conjugate base

(*e*)

$$\mathrm{(CH_3)_3CO^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{(CH_3)_3COH} + \mathrm{HO^-}$$

tert-Butoxide ion: base	Water: acid (stronger acid, $K_a \approx 10^{-16}$)	*tert*-Butyl alcohol: conjugate acid (weaker acid, $K_a \approx 10^{-18}$)	Hydroxide ion: conjugate base

(*f*)

$$\mathrm{(CH_3)_2CHOH} + \mathrm{H_2N^-} \rightleftharpoons \mathrm{(CH_3)_2CHO^-} + \mathrm{H_3N}$$

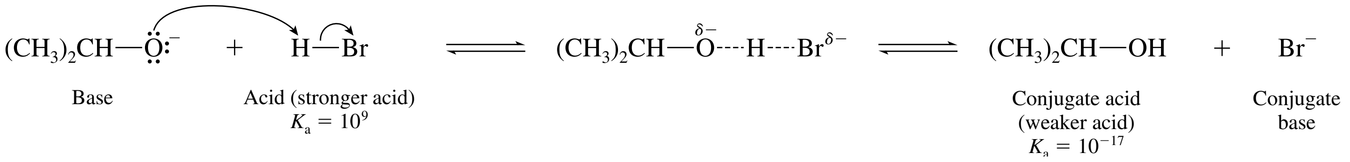
Isopropyl alcohol: acid (stronger acid, $K_a \approx 10^{-17}$)	Amide ion: base	Isopropoxide ion: conjugate base	Ammonia: conjugate acid (weaker acid, $K_a \approx 10^{-36}$)

(*g*)

$$\mathrm{F^-} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{HF} + \mathrm{HSO_4^-}$$

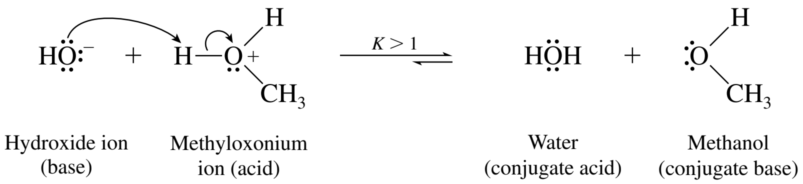
Fluoride ion: base	Sulfuric acid: acid (stronger acid, $K_a \approx 10^{5}$)	Hydrogen fluoride: conjugate acid (weaker acid, $K_a \approx 10^{-4}$)	Hydrogen sulfate ion: conjugate base

4.28 (*a*) The proton-transfer transition state can represent the following reaction, or its reverse:



When the reaction proceeds as drawn, the stronger acid (hydrogen bromide) is on the left, the weaker acid (isopropyl alcohol) is on the right, and the equilibrium lies to the right.

(*b*) Hydroxide is a strong base; methyloxonium ion is a strong acid.



4.29 (*a*) This problem reviews the relationship between logarithms and exponential numbers. We need to determine K_a, given pK_a. The equation that relates the two is

$$\mathrm{p}K_a = -\log_{10} K_a$$

Therefore

$$\begin{aligned} K_a &= 10^{-\mathrm{p}K_a} \\ &= 10^{-3.48} \\ &= 3.3 \times 10^{-4} \end{aligned}$$

(*b*) As described in part (*a*), $K_a = 10^{-pK_a}$, therefore K_a for vitamin C is given by the expression:

$$\begin{aligned} K_a &= 10^{-4.17} \\ &= 6.7 \times 10^{-5} \end{aligned}$$

(*c*) Similarly, $K_a = 1.8 \times 10^{-4}$ for formic acid (pK_a 3.75).

(*d*) $K_a = 6.5 \times 10^{-2}$ for oxalic acid (pK_a 1.19).

In ranking the acids in order of decreasing acidity, remember that the larger the equilibrium constant K_a, the stronger the acid; and the lower the pK_a value, the stronger the acid.

Acid	K_a	pK_a
Oxalic (strongest)	6.5×10^{-2}	1.19
Aspirin	3.3×10^{-4}	3.48
Formic acid	1.8×10^{-4}	3.75
Vitamin C (weakest)	6.7×10^{-5}	4.17

4.30 Because the pK_a of CH_3SH (11) is smaller than that of CH_3OH (16), CH_3SH is the stronger acid of the two. Its conjugate base (as in $KSCH_3$) is therefore weaker than the conjugate base of CH_3OH (as in $KOCH_3$).

4.31 This problem illustrates the reactions of a primary alcohol with the reagents described in the chapter.

(*a*) $$CH_3CH_2CH_2CH_2OH + NaNH_2 \longrightarrow CH_3CH_2CH_2CH_2O^-Na^+ + NH_3$$

Sodium butoxide

(*b*) $$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{HBr}} CH_3CH_2CH_2CH_2Br$$

1-Bromobutane

(*c*) $$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{NaBr, } H_2SO_4} CH_3CH_2CH_2CH_2Br$$

1-Bromobutane

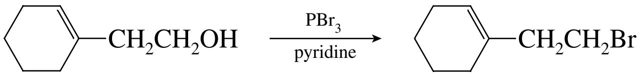
(*d*) $$CH_3CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2Br$$

1-Bromobutane

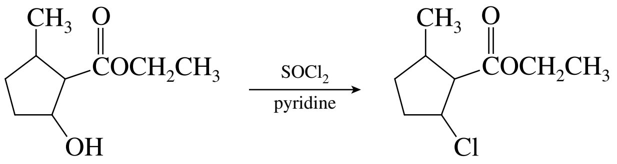
(*e*) $$CH_3CH_2CH_2CH_2OH \xrightarrow{SOCl_2} CH_3CH_2CH_2CH_2Cl$$

1-Chlorobutane

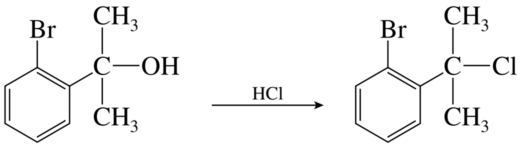
4.32 (*a*) This reaction was used to convert the primary alcohol to the corresponding bromide in 60% yield.



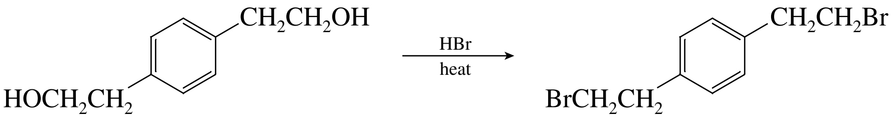
(*b*) Thionyl chloride treatment of this secondary alcohol gave the chloro derivative in 59% yield.



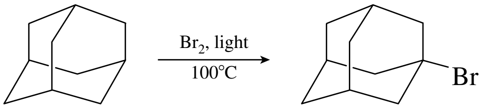
(*c*) The starting material is a tertiary alcohol and reacted readily with hydrogen chloride to form the corresponding chloride in 67% yield.



(*d*) Both primary alcohol functional groups were converted to primary bromides; the yield was 88%.



(*e*) This molecule is called adamantane. It has six equivalent CH_2 groups and four equivalent CH groups. Bromination is selective for tertiary hydrogens, so a hydrogen of one of the CH groups is replaced. The product shown was isolated in 76% yield.

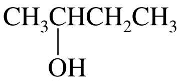
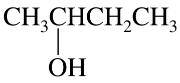
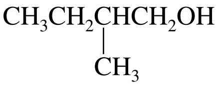
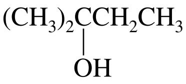
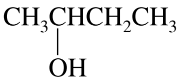


$C_{10}H_{15}Br$

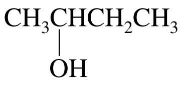
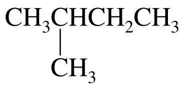
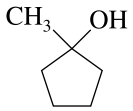
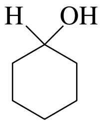
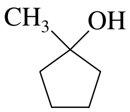
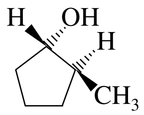
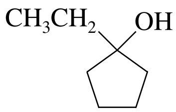
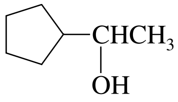
4.33 The order of reactivity of alcohols with hydrogen halides is tertiary > secondary > primary > methyl.

$$ROH + HBr \longrightarrow RBr + H_2O$$

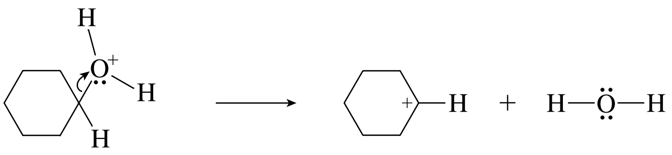
Reactivity of Alcohols with Hydrogen Bromide:

Part	More reactive	Less reactive
(*a*)	 $CH_3\underset{\substack{\vert \\ OH}}{C}HCH_2CH_3$ 2-Butanol: secondary	$CH_3CH_2CH_2CH_2OH$ 1-Butanol: primary
(*b*)	 $CH_3\underset{\substack{\vert \\ OH}}{C}HCH_2CH_3$ 2-Butanol: secondary	 $CH_3CH_2\underset{\substack{\vert \\ CH_3}}{C}HCH_2OH$ 2-Methyl-1-butanol: primary
(*c*)	 $(CH_3)_2\underset{\substack{\vert \\ OH}}{C}CH_2CH_3$ 2-Methyl-2-butanol: tertiary	 $CH_3\underset{\substack{\vert \\ OH}}{C}HCH_2CH_3$ 2-Butanol: secondary

(*continued*)

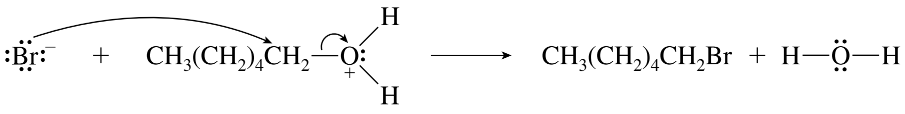
Part	More reactive	Less reactive
(*d*)	 $CH_3\underset{OH}{\underset{\mid}{C}}HCH_2CH_3$ 2-Butanol	 $CH_3\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_3$ 2-Methylbutane: not an alcohol; does not react with HBr
(*e*)	 1-Methylcyclopentanol: tertiary	 Cyclohexanol: secondary
(*f*)	 1-Methylcyclopentanol: tertiary	 *trans*-2-Methylcyclopentanol: secondary
(*g*)	 1-Ethylcyclopentanol: tertiary	 1-Cyclopentylethanol: secondary

4.34 The unimolecular step in the reaction of cyclohexanol with hydrogen bromide to give cyclohexyl bromide is the dissociation of the oxonium ion to a carbocation.



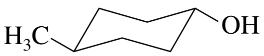
Cyclohexyloxonium ion Cyclohexyl cation Water

4.35 The nucleophile that attacks the oxonium ion in the reaction of 1-hexanol with hydrogen bromide is bromide ion.



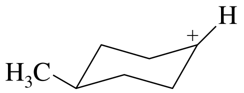
Bromide ion Hexyloxonium ion 1-Bromohexane Water

4.36 (*a*) Both the methyl group and the hydroxyl group are equatorial in the most stable conformation of *trans*-4-methylcyclohexanol.



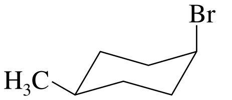
trans-4-Methylcyclohexanol

(*b*) The positively charged carbon in the carbocation intermediate is sp^2-hybridized, and is planar.

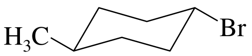


Carbocation intermediate

(*c*) Bromide ion attacks the carbocation from both above and below, giving rise to two stereoisomers, *cis*- and *trans*-1-bromo-4-methylcyclohexane.



cis-1-Bromo-4-methylcyclohexane



trans-1-Bromo-4-methylcyclohexane

4.37 Examine the equations to ascertain which bonds are made and which are broken. Then use the bond dissociation energies in Table 4.3 to calculate $\Delta H°$ for each reaction.

(*a*) $(CH_3)_2CH{-}OH + H{-}F \longrightarrow (CH_3)_2CH{-}F + H{-}OH$

$(CH_3)_2CH{-}OH$	$H{-}F$	$(CH_3)_2CH{-}F$	$H{-}OH$
385 kJ/mol (92 kcal/mol)	568 kJ/mol (136 kcal/mol)	439 kJ/mol (105 kcal/mol)	497 kJ/mol (119 kcal/mol)

Bond breaking: 953 kJ/mol (228 kcal/mol) Bond making: 936 kJ/mol (224 kcal/mol)

$$\begin{aligned}\Delta H° &= \text{energy cost of breaking bonds} - \text{energy given off in making bonds}\\ &= 953\text{ kJ/mol} - 936\text{ kJ/mol } (228\text{ kcal/mol} - 224\text{ kcal/mol})\\ &= +17\text{ kJ/mol } (+4\text{ kcal/mol})\end{aligned}$$

The reaction of isopropyl alcohol with hydrogen fluoride is endothermic.

(*b*) $(CH_3)_2CH{-}OH + H{-}Cl \longrightarrow (CH_3)_2CH{-}Cl + H{-}OH$

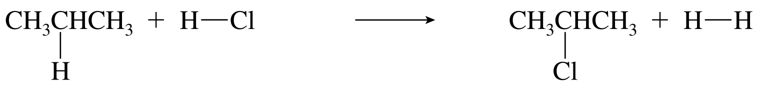
$(CH_3)_2CH{-}OH$	$H{-}Cl$	$(CH_3)_2CH{-}Cl$	$H{-}OH$
385 kJ/mol (92 kcal/mol)	431 kJ/mol (103 kcal/mol)	339 kJ/mol (81 kcal/mol)	497 kJ/mol (119 kcal/mol)

Bond breaking: 816 kJ/mol (195 kcal/mol) Bond making: 836 kJ/mol (200 kcal/mol)

$$\begin{aligned}\Delta H° &= \text{energy cost of breaking bonds} - \text{energy given off in making bonds}\\ &= 816\text{ kJ/mol} - 836\text{ kJ/mol } (195\text{ kcal/mol} - 200\text{ kcal/mol})\\ &= -20\text{ kJ/mol } (-5\text{ kcal/mol})\end{aligned}$$

The reaction of isopropyl alcohol with hydrogen chloride is exothermic.

(*c*)



$$CH_3\underset{\displaystyle H}{\underset{|}{C}}HCH_3 + H{-}Cl \longrightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 + H{-}H$$

C—H	H—Cl	C—Cl	H—H
397 kJ/mol (95 kcal/mol)	431 kJ/mol (103 kcal/mol)	339 kJ/mol (81 kcal/mol)	435 kJ/mol (104 kcal/mol)

Bond breaking: 828 kJ/mol (198 kcal/mol) Bond making: 774 kJ/mol (185 kcal/mol)

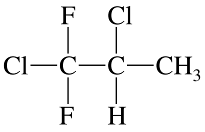
$$\begin{aligned}\Delta H° &= \text{energy cost of breaking bonds} - \text{energy given off in making bonds}\\ &= 828\text{ kJ/mol} - 774\text{ kJ/mol } (198\text{ kcal/mol} - 185\text{ kcal/mol})\\ &= +54\text{ kJ/mol } (+13\text{ kcal/mol})\end{aligned}$$

The reaction of propane with hydrogen chloride is endothermic.

4.38 In the statement of the problem you are told that the starting material is 2,2-dimethylpropane, that the reaction is one of fluorination, meaning that F_2 is a reactant, and that the product is $(CF_3)_4C$. You need to complete the equation by realizing that HF is also formed in the fluorination of alkanes. The balanced equation is therefore:

$$(CH_3)_4C + 12F_2 \longrightarrow (CF_3)_4C + 12HF$$

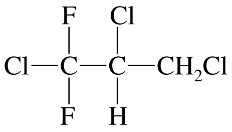
4.39 The reaction is free-radical chlorination, and substitution occurs at all possible positions that bear a replaceable hydrogen. Write the structure of the starting material, and identify the nonequivalent hydrogens.



$$\mathrm{Cl{-}\overset{F}{\underset{F}{C}}{-}\overset{Cl}{\underset{H}{C}}{-}CH_3}$$

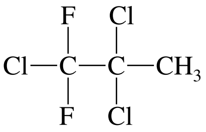
1,2-Dichloro-1,1-difluoropropane

The problem states that one of the products is 1,2,3-trichloro-1,1-difluoropropane. This compound arises by substitution of one of the methyl hydrogens by chlorine. We are told that the other product is an isomer of 1,2,3-trichloro-1,1-difluoropropane; therefore, it must be formed by replacement of the hydrogen at C-2.



$$\mathrm{Cl{-}\overset{F}{\underset{F}{C}}{-}\overset{Cl}{\underset{H}{C}}{-}CH_2Cl}$$

1,2,3-Trichloro-1,1-difluoropropane

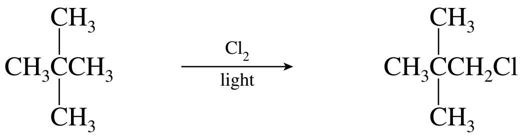


$$\mathrm{Cl{-}\overset{F}{\underset{F}{C}}{-}\overset{Cl}{\underset{Cl}{C}}{-}CH_3}$$

1,2,2-Trichloro-1,1-difluoropropane

4.40 Free-radical chlorination leads to substitution at each carbon that bears a hydrogen. This problem essentially requires you to recognize structures that possess various numbers of nonequivalent hydrogens. The easiest way to determine the number of constitutional isomers that can be formed by chlorination of a particular compound is to replace one hydrogen with chlorine and assign an IUPAC name to the product. Continue by replacing one hydrogen on each carbon in the compound, and compare names to identify duplicates.

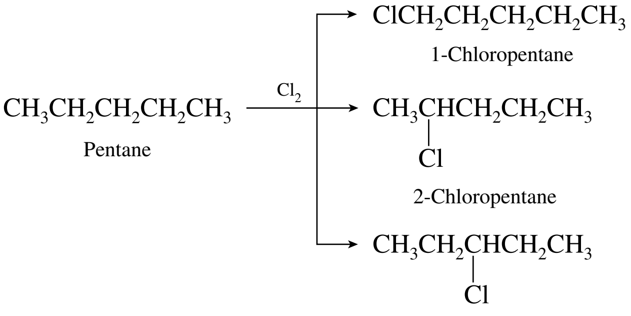
(*a*) 2,2-Dimethylpropane is the C_5H_{12} isomer that gives a single monochloride, since all the hydrogens are equivalent.



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3 \xrightarrow[light]{Cl_2} CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2Cl}$$

2,2-Dimethylpropane 1-Chloro-2,2-dimethylpropane

(*b*) The C_5H_{12} isomer that has three nonequivalent sets of hydrogens is pentane. It yields three isomeric monochlorides on free-radical chlorination.



$$\mathrm{CH_3CH_2CH_2CH_2CH_3 \xrightarrow{Cl_2} ClCH_2CH_2CH_2CH_2CH_3 + CH_3\underset{Cl}{C}HCH_2CH_2CH_3 + CH_3CH_2\underset{Cl}{C}HCH_2CH_3}$$

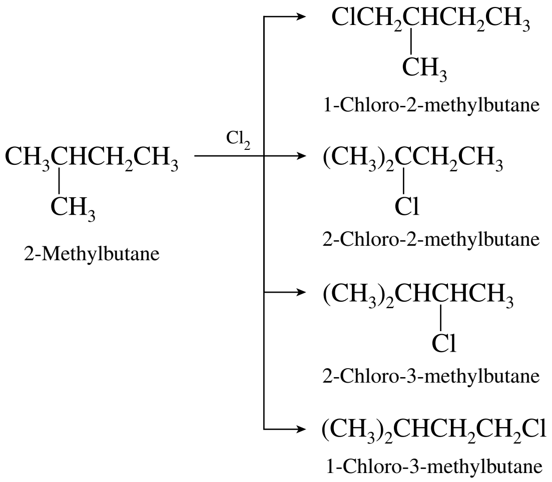
Pentane

1-Chloropentane

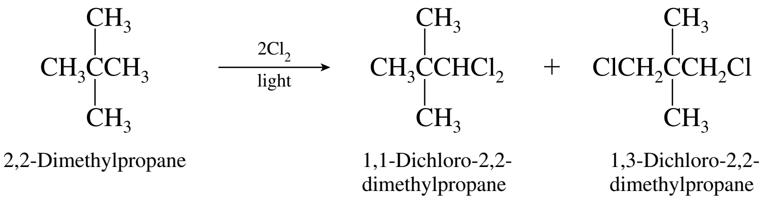
2-Chloropentane

3-Chloropentane

(*c*) 2-Methylbutane forms four different monochlorides.



(*d*) For only two dichlorides to be formed, the starting alkane must have a structure that is rather symmetrical; that is, one in which most (or all) of the hydrogens are equivalent. 2,2-Dimethylpropane satisfies this requirement.



4.41 (*a*) Heptane has five methylene groups, which on chlorination together contribute 85% of the total monochlorinated product.

$$\mathrm{CH_3(CH_2)_5CH_3} \longrightarrow \underset{15\%}{\mathrm{CH_3(CH_2)_5CH_2Cl}} + \underset{85\%}{(\text{2-chloro} + \text{3-chloro} + \text{4-chloro})}$$

Since the problem specifies that attack at each methylene group is equally probable, the five methylene groups each give rise to 85/5, or 17%, of the monochloride product.

Since C-2 and C-6 of heptane are equivalent, we calculate that 2-chloroheptane will constitute 34% of the monochloride fraction. Similarly, C-3 and C-5 are equivalent, and so there should be 34% 3-chloroheptane. The remainder, 17%, is 4-chloroheptane.

These predictions are very close to the observed proportions.

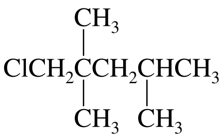
	Calculated, %	Observed, %
2-Chloro	34	35
3-Chloro	34	34
4-Chloro	17	16

(*b*) There are a total of 20 methylene hydrogens in dodecane, $CH_3(CH_2)_{10}CH_3$. The 19% 2-chlorododecane that is formed arises by substitution of any of the four equivalent methylene hydrogens at C-2 and C-11. The total amount of substitution of methylene hydrogens must therefore be:

$$\frac{20}{4} \times 19\% = 95\%$$

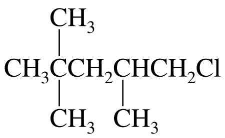
The remaining 5% corresponds to substitution of methyl hydrogens at C-1 and C-12. The proportion of 1-chlorododecane in the monochloride fraction is 5%.

4.42 (*a*) Two of the monochlorides derived from chlorination of 2,2,4-trimethylpentane are primary chlorides:



$$\mathrm{ClCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}HCH_3}$$

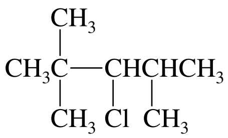
1-Chloro-2,2,4-trimethylpentane



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}HCH_2Cl}$$

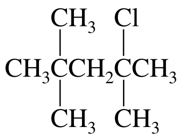
1-Chloro-2,4,4-trimethylpentane

The two remaining isomers are a secondary chloride and a tertiary chloride:



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}{-}\underset{Cl}{C}H\underset{CH_3}{C}HCH_3}$$

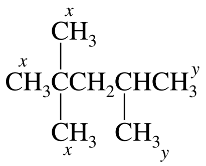
3-Chloro-2,2,4-trimethylpentane



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{Cl}{\underset{CH_3}{C}}CH_3}$$

2-Chloro-2,4,4-trimethylpentane

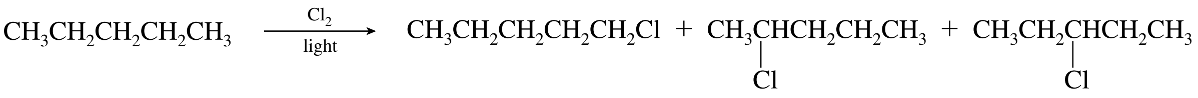
(*b*) Substitution of any one of the nine hydrogens designated as *x* in the structural diagram yields 1-chloro-2,2,4-trimethylpentane. Substitution of any one of the six hydrogens designated as *y* gives 1-chloro-2,4,4-trimethylpentane.



$$\mathrm{\overset{x}{C}H_3\overset{\overset{x}{CH_3}}{\underset{\underset{x}{CH_3}}{C}}CH_2\underset{\underset{y}{CH_3}}{C}HCH_3^{\,y}}$$

Assuming equal reactivity of a single *x* hydrogen and a single *y* hydrogen, the ratio of the two isomers is then expected to be 9 : 6. Since together the two primary chlorides total 65% of the monochloride fraction, there will be 39% 1-chloro-2,2,4-trimethylpentane (substitution of *x*) and 26% 1-chloro-2,4,4-trimethylpentane (substitution of *y*).

4.43 The three monochlorides are shown in the equation

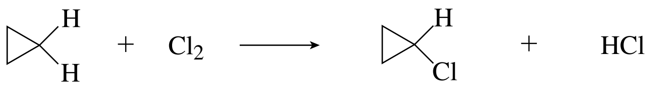


$$\mathrm{CH_3CH_2CH_2CH_2CH_3 \xrightarrow[light]{Cl_2} CH_3CH_2CH_2CH_2CH_2Cl + CH_3\underset{Cl}{C}HCH_2CH_2CH_3 + CH_3CH_2\underset{Cl}{C}HCH_2CH_3}$$

Pentane 1-Chloropentane 2-Chloropentane 3-Chloropentane

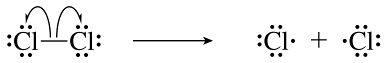
Pentane has six primary hydrogens (two CH_3 groups) and six secondary hydrogens (three CH_2 groups). Since a single secondary hydrogen is abstracted three times faster than a single primary hydrogen and there are equal numbers of secondary and primary hydrogens, the product mixture should contain three times as much of the secondary chloride isomers as the primary chloride. The primary chloride 1-chloropentane, therefore, is expected to constitute 25% of the product mixture. The secondary chlorides 2-chloropentane and 3-chloropentane are not formed in equal amounts. Rather, 2-chloropentane may be formed by replacement of a hydrogen at C-2 or at C-4, whereas 3-chloropentane is formed only when a C-3 hydrogen is replaced. The amount of 2-chloropentane is therefore 50%, and that of 3-chloropentane is 25%. We predict the major product to be 2-chloropentane, and the predicted proportion of 50% corresponds closely to the observed 46%.

4.44 The equation for the reaction is



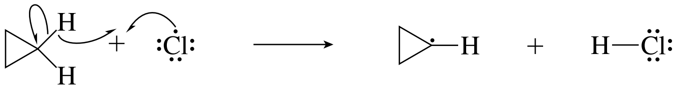
Cyclopropane Chlorine Cyclopropyl chloride Hydrogen chloride

The reaction begins with the initiation step in which a chlorine molecule dissociates to two chlorine atoms.



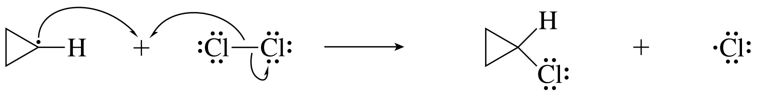
Chlorine 2 Chlorine atoms

A chlorine atom abstracts a hydrogen atom from cyclopropane in the first propagation step.



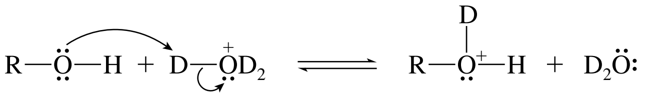
Cyclopropane Chlorine atom Cyclopropyl radical Hydrogen chloride

Cyclopropyl radical reacts with Cl_2 in the next propagation step.

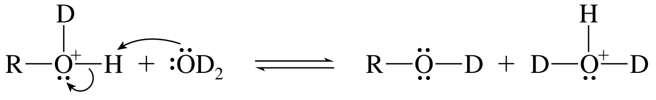


Cyclopropyl radical Chlorine Cyclopropyl chloride Chlorine atom

4.45 (*a*) Acid-catalyzed hydrogen–deuterium exchange takes place by a pair of Brønsted acid–base reactions.

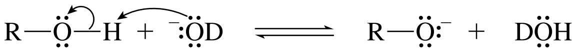


Base Acid Conjugate acid Conjugate base

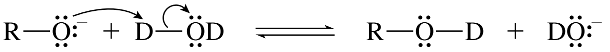


Acid Base Conjugate base Conjugate acid

(*b*) Base-catalyzed hydrogen–deuterium exchange occurs by a different pair of Brønsted acid–base equilibria.



Acid Base Conjugate base Conjugate acid



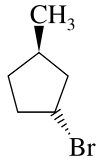
Base Acid Conjugate acid Conjugate base

SELF-TEST

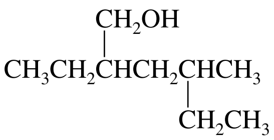
PART A

A-1. Give the correct substitutive IUPAC name for each of the following compounds:

(*a*)



(*b*)

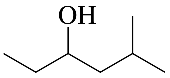


$$CH_3CH_2\overset{CH_2OH}{\overset{|}{C}}HCH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_3$$

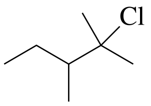
A-2. Draw the structures of the following substances:
- (*a*) 2-Chloro-1-iodo-2-methylheptane
- (*b*) *cis*-3-Isopropylcyclohexanol

A-3. Give both a functional class and a substitutive IUPAC name for each of the following compounds:

(*a*)



(*b*)

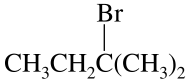


A-4. What are the structures of the conjugate acid and the conjugate base of CH_3OH?

A-5. Supply the missing component for each of the following reactions:

(*a*) $$CH_3CH_2CH_2OH \xrightarrow{SOCl_2} ?$$

(*b*)



$$? \xrightarrow{HBr} CH_3CH_2\overset{Br}{\overset{|}{C}}(CH_3)_2$$

A-6. (*a*) Write the products of the acid–base reaction that follows, and identify the stronger acid and base and the conjugate of each. Will the equilibrium lie to the left ($K < 1$) or to the right ($K > 1$)? The approximate pK_a of NH_3 is 36; that of CH_3CH_2OH is 16.

$$CH_3CH_2O^- + NH_3 \rightleftharpoons$$

(*b*) Draw a representation of the transition state of the elementary step of the reaction in part (*a*).

A-7. (*a*) How many different free radicals can possibly be produced in the reaction between chlorine atoms and 2,4-dimethylpentane?
(*b*) Write their structures.
(*c*) Which is the most stable? Which is the least stable?

A-8. Write a balanced chemical equation for the reaction of chlorine with the pentane isomer that gives only one product on monochlorination.

A-9. Write the propagation steps for the light-initiated reaction of bromine with methylcyclohexane.

A-10. Using the data in Table B-1 of this Study Guide, calculate the heat of reaction ($\Delta H°$) for the light-initiated reaction of bromine (Br_2) with 2-methylpropane to give 2-bromo-2-methylpropane and hydrogen bromide.

A-11. (*a*) Write out each of the elementary steps in the reaction of *tert*-butyl alcohol with hydrogen bromide. Use curved arrows to show electron movement in each step.
(*b*) Draw the structure of the transition state representing the unimolecular dissociation of the alkyloxonium ion in the preceding reaction.

(*c*) How does the mechanism of the reaction between 1-butanol and hydrogen bromide differ from the reaction in part (*a*)?

A-12. (Choose the correct response for each part.) Which species or compound:

(*a*) Reacts faster with sodium bromide and sulfuric acid?

2-methyl-3-pentanol or 3-methyl-3-pentanol

(*b*) Is a stronger base?

$KOC(CH_3)_3$ or $HOC(CH_3)_3$

(*c*) Reacts more vigorously with cyclohexane?

Fluorine or iodine

(*d*) Has an odd number of electrons?

Ethoxide ion or ethyl radical

(*e*) Undergoes bond cleavage in the initiation step in the reaction by which methane is converted to chloromethane?

CH_4 or Cl_2

PART B

B-1. A certain alcohol has the functional class IUPAC name **1-ethyl-3-methylbutyl alcohol.** What is its substitutive name?

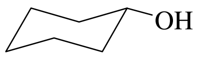
(*a*) 1-Ethyl-3-methyl-1-butanol
(*b*) 2-Methyl-1-hexanol
(*c*) 3-Methyl-1-hexanol
(*d*) 2-Methyl-4-hexanol
(*e*) 5-Methyl-3-hexanol

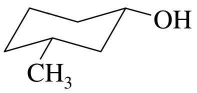
B-2. Rank the following substances in order of increasing boiling point (lowest → highest):

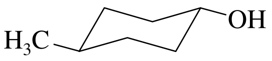
$CH_3CH_2CH_2CH_2OH$	$(CH_3)_2CHOCH_3$	$(CH_3)_3COH$	$(CH_3)_4C$
1	2	3	4

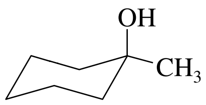
(*a*) $1 < 3 < 2 < 4$
(*b*) $2 < 4 < 3 < 1$
(*c*) $4 < 2 < 3 < 1$
(*d*) $2 < 3 < 1 < 4$
(*e*) $4 < 3 < 2 < 1$

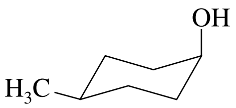
B-3. Which one of the following reacts with HBr at the fastest rate?

(*a*)


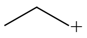
(*c*)


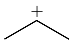
(*e*)


(*b*)


(*d*)


B-4. What is the decreasing stability order (most stable → least stable) of the following carbocations?


1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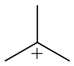
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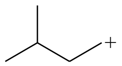
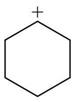
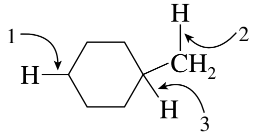

4


5

(*a*) $3 > 2 > 1 > 4 > 5$
(*b*) $1 \approx 4 > 2 \approx 5 > 3$
(*c*) $3 > 2 \approx 5 > 1 \approx 4$
(*d*) $3 > 1 \approx 4 > 2 \approx 5$

B-5. Rank the bond dissociation energies (BDEs) of the bonds indicated with the arrows from smallest to largest.

(*a*) 1 < 2 < 3
(*b*) 3 < 2 < 1
(*c*) 2 < 3 < 1
(*d*) 1 < 3 < 2
(*e*) 3 < 1 < 2



B-6. What are the chain-propagating steps in the free-radical chlorination of methane?

1. $Cl_2 \longrightarrow 2Cl\cdot$
2. $Cl\cdot + CH_4 \longrightarrow CH_3Cl + H\cdot$
3. $Cl\cdot + CH_4 \longrightarrow \cdot CH_3 + HCl$
4. $H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$
5. $\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$
6. $\cdot CH_3 + CH_4 \longrightarrow CH_4 + \cdot CH_3$

(*a*) 2, 4 (*b*) 1, 2 (*c*) 3, 5 (*d*) 1, 3, 5
(*e*) A combination different from those listed

B-7. Which of the following is *least* able to serve as a nucleophile in a chemical reaction?
(*a*) Br^- (*b*) OH^- (*c*) NH_3 (*d*) $CH_3{}^+$

B-8. Thiols are alcohol analogs in which the oxygen has been replaced by sulfur (e.g., CH_3SH). Given the fact that the S—H bond is less polar than the O—H bond, which of the following statements comparing thiols and alcohols is correct?
(*a*) Hydrogen bonding forces are weaker in thiols.
(*b*) Hydrogen bonding forces are stronger in thiols.
(*c*) Hydrogen bonding forces would be the same.
(*d*) No comparison can be made without additional information.

B-9. Rank the **transition states** that occur during the following reaction steps in order of increasing stability (least → most stable):

1. $CH_3—\overset{+}{O}H_2 \longrightarrow CH_3{}^+ + H_2O$
2. $(CH_3)_3C—\overset{+}{O}H_2 \longrightarrow (CH_3)_3C^+ + H_2O$
3. $(CH_3)_2CH—\overset{+}{O}H_2 \longrightarrow (CH_3)_2CH^+ + H_2O$

(*a*) 1 < 2 < 3 (*b*) 2 < 3 < 1 (*c*) 1 < 3 < 2 (*d*) 2 < 1 < 3

B-10. Using the data from Appendix B (Table B-1), calculate the heat of reaction $\Delta H°$ for the following:

$$CH_3CH_2\cdot + HBr \longrightarrow CH_3CH_3 + Br\cdot$$

(*a*) +69 kJ/mol (+16.5 kcal/mol)
(*b*) −69 kJ/mol (−16.5 kcal/mol)
(*c*) +44 kJ/mol (+10.5 kcal/mol)
(*d*) −44 kJ/mol (−10.5 kcal/mol)

B-11. An alkane with a molecular formula C_6H_{14} reacts with chlorine in the presence of light and heat to give **four** constitutionally isomeric monochlorides of molecular formula $C_6H_{13}Cl$. What is the most reasonable structure for the starting alkane?
(*a*) $CH_3CH_2CH_2CH_2CH_2CH_3$
(*b*) $(CH_3)_2CHCH_2CH_2CH_3$
(*c*) $CH_3CH(CH_2CH_3)_2$
(*d*) $(CH_3)_3CCH_2CH_3$
(*e*) $(CH_3)_2CHCH(CH_3)_2$

B-12. The species shown in the box represents ______ of the reaction between isopropyl alcohol and hydrogen bromide.

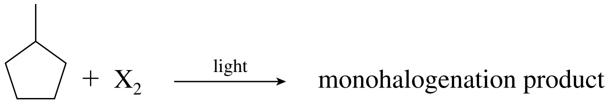
$$\boxed{(CH_3)_2\overset{\delta+}{C}H\text{-------}\overset{\delta+}{O}H_2}$$

(*a*) the alkyloxonium ion intermediate

(*b*) the transition state of the bimolecular proton transfer step

(*c*) the transition state of the capture of the carbocation by a nucleophile
(*d*) the carbocation intermediate
(*e*) the transition state of the unimolecular dissociation step

For the remaining four questions, consider the following free-radical reaction:



B-13. Light is involved in which of the following reaction steps?
(*a*) Initiation only
(*b*) Propagation only
(*c*) Termination only
(*d*) Initiation and propagation

B-14. Which of the following statements about the reaction is *not* true?
(*a*) Halogen atoms are consumed in the first propagation step.
(*b*) Halogen atoms are regenerated in the second propagation step.
(*c*) Hydrogen atoms are produced in the first propagation step.
(*d*) Chain termination occurs when two radicals react with each other.

B-15. How many monohalogenation products are possible. (Do not consider stereoisomers.)
(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 5

B-16. Which halogen (X_2) will give the best yield of a single monohalogenation product?
(*a*) F_2 (*b*) Cl_2 (*c*) Br_2 (*d*) I_2