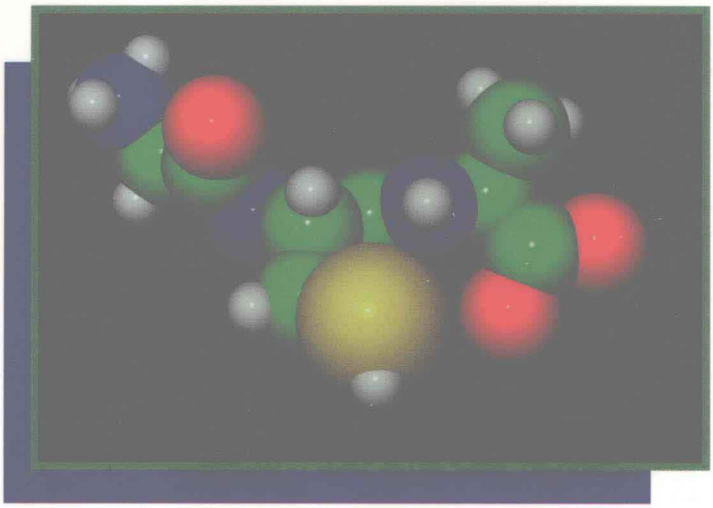
Solutions Manual

Jan William Simek



Organic Chemistry

Third Edition

L.G. Wade, Jr.

SOLUTIONS MANUAL

Jan William Simek

Organic Chemistry

Third Edition

L.G. Wade, Jr.

Prentice Hall, Upper Saddle River, New Jersey 07458

Editorial/ production supervision: ***Amy Jolin***
Manufacturing coordinator: ***Trudy Pisciotti***
Supplements Acquisitions editor: ***Mary Hornby***

Simon & Schuster Company / A Viacom Company
Upper Saddle River, New Jersey 07458

Printed in the United States of America

10 9 8 7 6 5 4

ISBN: 0-13-324773-2

PRENTICE-HALL INTERNATIONAL (UK) LIMITED, LONDON
PRENTICE-HALL OF AUSTRALIA PTY. LIMITED, SYDNEY
PRENTICE-HALL CANADA INC. TORONTO
PRENTICE-HALL HISPANOAMERICANA, S.A., MEXICO
PRENTICE-HALL OF INDIA PRIVATE LIMITED, NEW DELHI
PRENTICE-HALL OF JAPAN, INC., TOKYO
SIMON & SCHUSTER ASIA PTE. LTD., SINGAPORE
EDITORA PRENTICE-HALL DO BRASIL, LTDA., RIO DE JANEIRO

SOLUTIONS MANUAL

Organic Chemistry

PREFACE

Including "Hints for Passing Organic Chemistry"

Do you want to pass your course in organic chemistry? Here is my best advice, based on twenty-plus years of observing students learning organic chemistry:

Hint #1: *Do the problems.* It seems straightforward, but humans, including students, try to take the easy way out until they discover there is no short-cut. Unless you have a measured IQ above 200 and comfortably cruise in the top 1% of your class, *do the problems.* Usually your teacher (professor or teaching assistant) will recommend certain ones; try to do all those recommended. If you do half of them, you will be half-prepared come test time. (Do you want your surgeon coming to your appendectomy having practiced only *half* the procedure?) And when you do the problems, keep this Solutions Manual CLOSED. Avoid looking at *my* answer before you write *your* answer—your trying and struggling with the problem is the most valuable part of the problem. Remember that the primary goal of doing these problems is *not* just getting the right answer, but understanding the material well enough to get right answers to the questions you haven't seen yet.

Hint #2: *Keep up.* Getting behind in your work in a course that moves as quickly as this one is the Kiss of Death. For most students, organic chemistry is the most rigorous intellectual challenge they have faced so far in their studies. Some are taken by surprise at the diligence it requires. Don't think that you can study all of the material the couple of days before the exam—well, you can, but you won't pass. Study organic chemistry like a foreign language: try to do some every day so that the freshly-trained neurons stay sharp.

Hint #3: *Get help when you need it.* Use your teacher's office hours when you have difficulty. Many schools have tutoring centers (in which organic chemistry is a popular offering). Here's a secret: absolutely the best way to cement this material in your brain is to get together with a few of your fellow students and make up problems for each other, then correct and discuss them. When *you* write the problems, you will gain great insight into what this is all about.

So what is the point of this Solutions Manual? First, I can't do your studying for you. Second, since I am not leaning over your shoulder as you write your answers, I can't give you direct feedback on what you write and think—the print medium is limited in its usefulness. What I *can* do for you is: 1) provide correct answers; the publishers, Professor Wade, Ms. Meisenheimer (my reviewer), and I have gone to great lengths to assure that what I have written is correct, for we all understand how it can shake a student's confidence to discover that the answer book flubbed up; 2) provide a considerable degree of rigor; beyond the fundamental requirement of correctness, I have tried to flesh out these answers, being complete but succinct; 3) provide insight into how to solve a problem and into where the sticky intellectual points are. Insight is the toughest to accomplish, but over the years, I have come to understand where students have trouble, so I have tried to anticipate your questions and to add enough detail so that the concept, as well as the answer, is clear.

It is difficult for students to understand or acknowledge that their teachers are human (some are more human than others). Since I am human (despite what my students might report), I can and do make mistakes. If there are mistakes in this book, they are my sole responsibility, and I am sorry. If you find one, PLEASE let me know so that it can be corrected in future printings. Nip it in the bud.

Acknowledgments

No project of this scope is ever done alone. These are team efforts, and there are several people who have assisted and facilitated in one fashion or another who deserve my thanks.

Professor L. G. Wade is a remarkable person. He has gone to extraordinary lengths to make the textbook as clear, organized, informative and insightful as possible. He has solicited and followed my suggestions on his text, and his comments on my solutions have been perceptive and valuable. We agreed early on that our primary goal is to help the students learn a fascinating and challenging subject, and all of our efforts have been directed toward that goal. I have appreciated our collaboration.

My former student, current friend and colleague, and soon-to-be Dr., Kristen Meisenheimer, has reviewed every problem and every solution. Her precision, diligence, and sensitivity (and diplomacy!) have made this a much better supplement. I will be forever grateful for her enthusiasm, wisdom, and devotion.

The people at Prentice-Hall have made this project possible. Good books would not exist without their dedication, professionalism, and experience. Among the many people who contributed are: Lee Englander, who connected me with this project; Deirdre Cavanaugh, Chemistry Editor; and Mary Hornby, Supplements Editor.

With the small exception of the NMR spectra, the entire manuscript was produced using *ChemDraw Plus®*, the remarkable software for drawing chemical structures developed by Cambridge Scientific Computing, Inc., Cambridge, MA. We, the users of sophisticated software like ChemDraw, are the beneficiaries of the intelligence and creativity of the people in the computer industry. I am fortunate that they are so smart.

Finally, I appreciate my friends who supported me throughout this project. The students are too numerous to list, but it is for them that all this happens.

Jan William Simek
Chemistry Department
Cal Poly State University
San Luis Obispo, CA 93407
Internet: jsimek@cymbal.aix.calpoly.edu

DEDICATION

To my inspirational chemistry teachers:

Joe Plaskas, who made the batter;

Kurt Kaufman, who baked the cake;

Carl Djerassi, who put on the icing;

and to my parents:

Ervin J. and Imilda B. Simek,

who had the original concept.

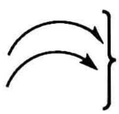
SYMBOLS AND ABBREVIATIONS

Below is a list of symbols and abbreviations used in this Solutions Manual, consistent with those used in the textbook by Wade. (Do not expect all of these to make sense to you now. You will learn them throughout your study of organic chemistry.)

BONDS

—	a single bond
=	a double bond
≡	a triple bond
(wedge)	a bond in three dimensions, coming out of the paper toward the reader
(hashed)	a bond in three dimensions, going behind the paper away from the reader
- - - - - -	a stretched bond, in the process of forming or breaking

ARROWS

→	in a reaction, shows direction from reactants to products
⇌	signifies equilibrium (not to be confused with resonance)
↔	signifies resonance (not to be confused with equilibrium)
	shows direction of electron movement: the arrowhead with one barb shows movement of one electron; the arrowhead with two barbs shows movement of a pair of electrons
+→	shows polarity of a bond or molecule, the arrowhead signifying the more negative end of the dipole

SUBSTITUENT GROUPS

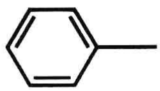
Me	a methyl group, CH_3
Et	an ethyl group, CH_2CH_3
Pr	a propyl group, a three carbon group (two possible arrangements)
Bu	a butyl group, a four carbon group (four possible arrangements)
R	the general abbreviation for an alkyl group (or any substituent group not under scrutiny)

continued on next page

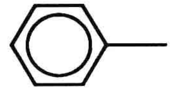
Symbols and Abbreviations, continued

SUBSTITUENT GROUPS, continued

Ph a phenyl group, the name of a benzene ring as a substituent, represented:

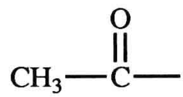


or

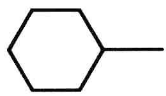


Ar the general name for an aromatic group

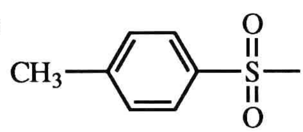
Ac an acetyl group:



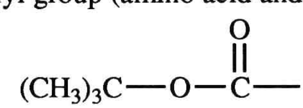
Cy a cyclohexyl group:



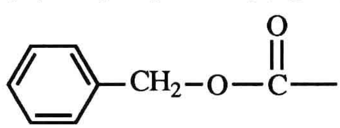
Ts tosyl, or *p*-toluenesulfonyl group:



Boc a *t*-butoxycarbonyl group (amino acid and peptide chemistry):

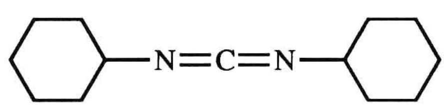


Z, or Cbz a carbobenzoxy (benzyloxycarbonyl) group (amino acid and peptide chemistry):

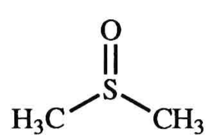


REAGENTS AND SOLVENTS

DCC **dicyclohexylcarbodiimide**



DMSO **dimethylsulfoxide**



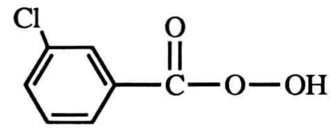
continued on next page

Symbols and Abbreviations, continued

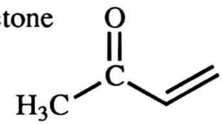
REAGENTS AND SOLVENTS, continued

ether diethyl ether, $CH_3CH_2OCH_2CH_3$

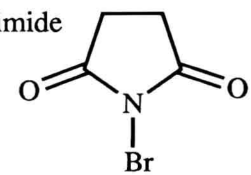
MCPBA *meta*-chloroperoxybenzoic acid



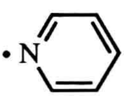
MVK methyl vinyl ketone



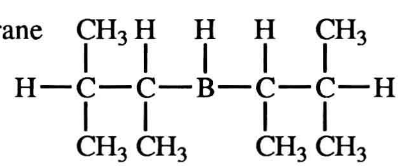
NBS *N*-bromosuccinimide



PCC pyridinium chlorochromate, CrO_3 • HCl •



Sia_2BH disiamylborane



THF tetrahydrofuran

SPECTROSCOPY

IR infrared spectroscopy

NMR nuclear magnetic resonance spectroscopy

MS mass spectrometry

UV ultraviolet spectroscopy

ppm parts per million, a unit used in NMR

continued on next page

SPECTROSCOPY, continued

Hz	hertz, cycles per second, a unit of frequency
MHz	megahertz, millions of cycles per second
TMS	**t**etra**m**ethyl**s**ilane, $(CH_3)_4Si$, the reference compound in NMR
s, d, t, q	**s**inglet, **d**oublet, **t**riplet, **q**uartet, referring to the number of peaks an NMR absorption gives
nm	nanometers, 10^{-9} meters (usually used as a unit of wavelength)
m/z	mass-to-charge ratio, in mass spectrometry
δ	in NMR, chemical shift value, measured in ppm
λ	wavelength
ν	frequency

OTHER

a, ax	axial (in chair forms of cyclohexane)
e, eq	equatorial (in chair forms of cyclohexane)
HOMO	**h**ighest **o**ccupied **m**olecular **o**rbital
LUMO	**l**owest **u**noccupied **m**olecular **o**rbital
NR	no reaction
o, m, p	*ortho, meta, para* (positions on an aromatic ring)
Δ	when written over an arrow: "heat" when written before a letter: "change in"
δ^+, δ^-	partial positive charge, partial negative charge
$h\nu$	energy from electromagnetic radiation (light)
$[\alpha]_D$	specific rotation at the D line of sodium (589 nm)

TABLE OF CONTENTS

Preface

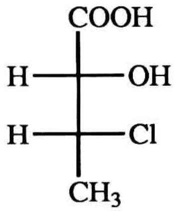
Symbols and Abbreviations

Chapter 1 Introduction and Review 1
Chapter 2 Structure and Properties of Organic Molecules 30
Chapter 3 Structure and Stereochemistry of Alkanes 53
Chapter 4 The Study of Chemical Reactions 69
Chapter 5 Stereochemistry 90
Chapter 6 Alkyl Halides: Nucleophilic Substitution and Elimination 111
Chapter 7 Structure and Synthesis of Alkenes 153
Chapter 8 Reactions of Alkenes 175
Chapter 9 Structure and Synthesis of Alcohols 207
Chapter 10 Reactions of Alcohols 226
Chapter 11 Infrared Spectroscopy and Mass Spectrometry 255
Chapter 12 Nuclear Magnetic Resonance Spectroscopy 266
Chapter 13 Ethers and Epoxides 297
Chapter 14 Alkynes 319
Chapter 15 Conjugated Systems, Orbital Symmetry, and Ultraviolet Spectroscopy 345
Chapter 16 Aromatic Compounds 370
Chapter 17 Reactions of Aromatic Compounds 396
Chapter 18 Ketones and Aldehydes 438
Chapter 19 Amines 475
Chapter 20 Carboxylic Acids 508
Chapter 21 Carboxylic Acid Derivatives 535
Chapter 22 Additions and Condensations of Enols and Enolate Ions 578
Chapter 23 Carbohydrates and Nucleic Acids 640
Chapter 24 Amino Acids, Peptides, and Proteins 676
Chapter 25 Lipids 706
Chapter 26 Synthetic Polymers 720

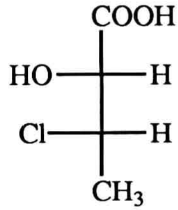
Appendix: Summary of IUPAC Nomenclature 738

5-21

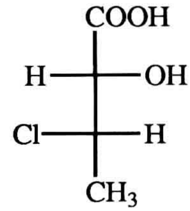
(a)



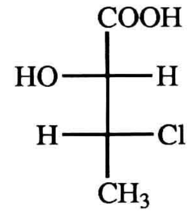
A



B



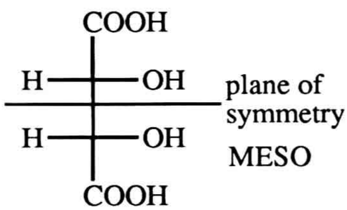
C



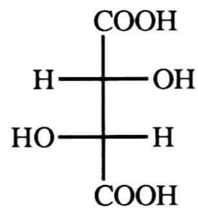
D

enantiomers: A and B; C and D
diastereomers: A and C, A and D, B and C, B and D

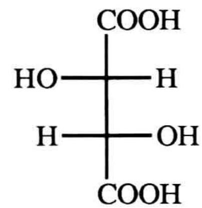
(b)



E



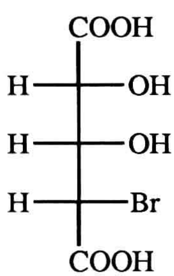
F



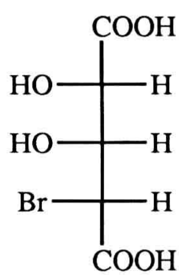
G

enantiomers: F and G
diastereomers: E and F, E and G

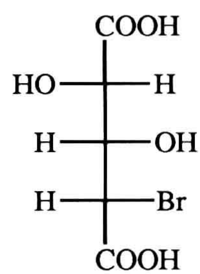
(c)



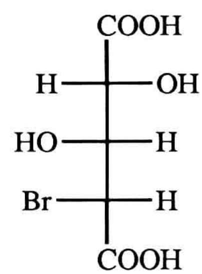
H



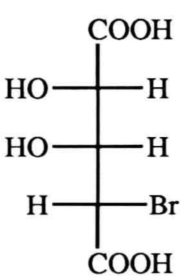
I



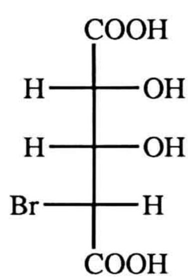
J



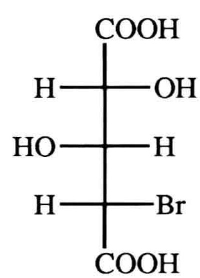
K



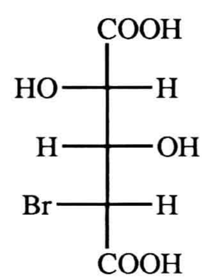
L



M



N

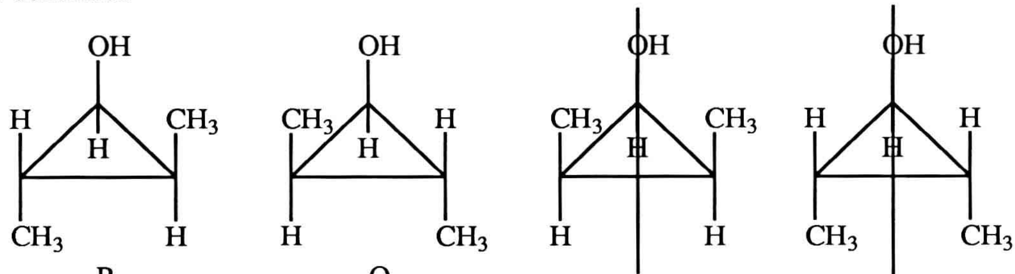


O

enantiomers: H and I, J and K, L and M, N and O
diastereomers: any pair which is not enantiomeric

5-21 continued

(d)



P Q

plane of symmetry MESO T

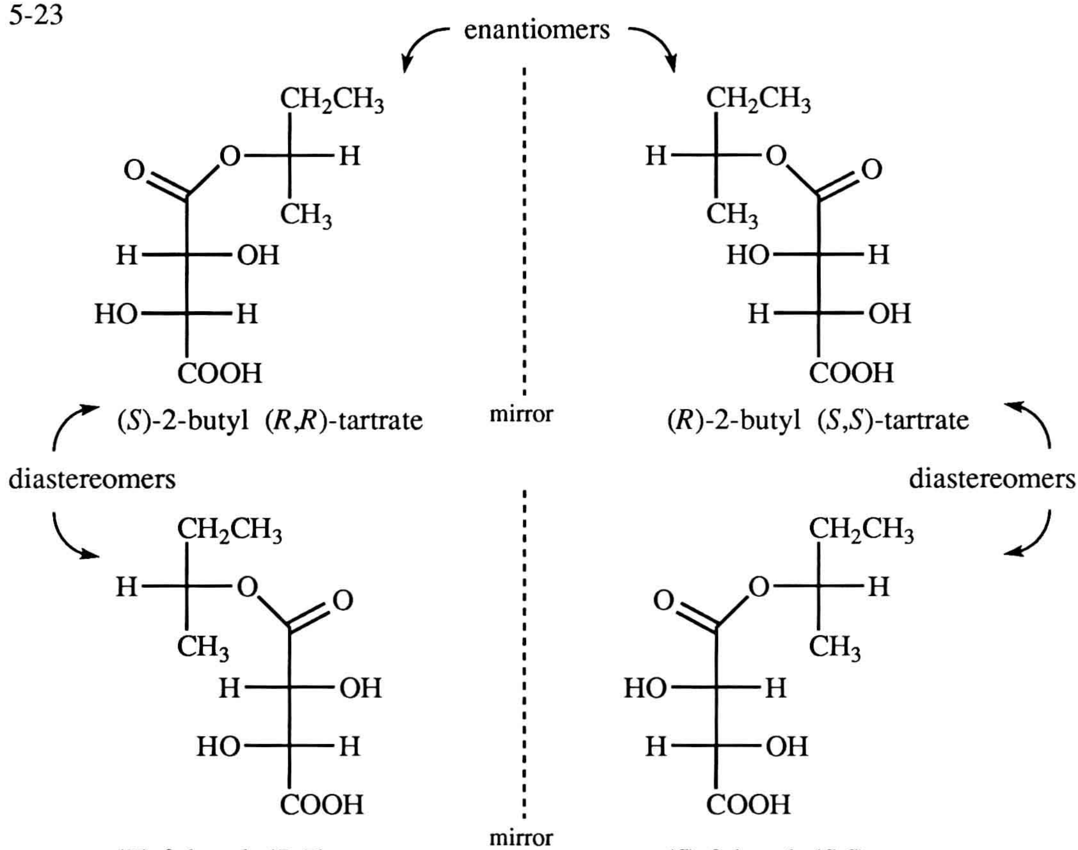
plane of symmetry MESO U

enantiomers: P and Q
diastereomers: P and T, P and U, Q and T, Q and U, T and U

5-22

Any diastereomeric pair could be separated by a physical process like distillation or crystallization. Diastereomers are found in parts (a), (b), and (d). The structures in (c) are enantiomers; they could not be separated by normal physical means.

5-23



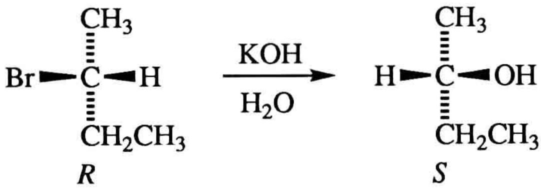
(*S*)-2-butyl (*R*,*R*)-tartrate

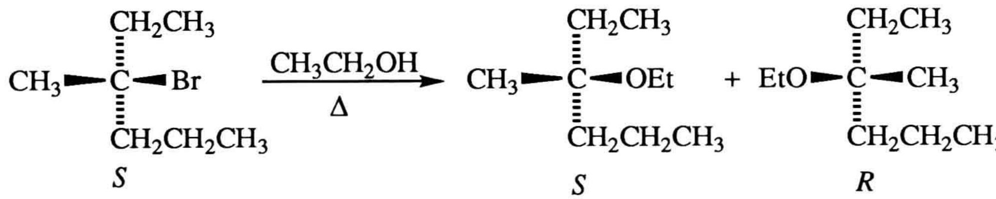
(*R*)-2-butyl (*S*,*S*)-tartrate

(*R*)-2-butyl (*R*,*R*)-tartrate

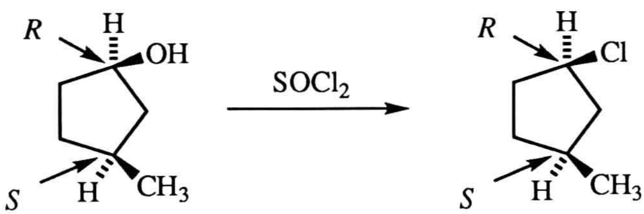
(*S*)-2-butyl (*S*,*S*)-tartrate

5-24

(a)  inversion of configuration

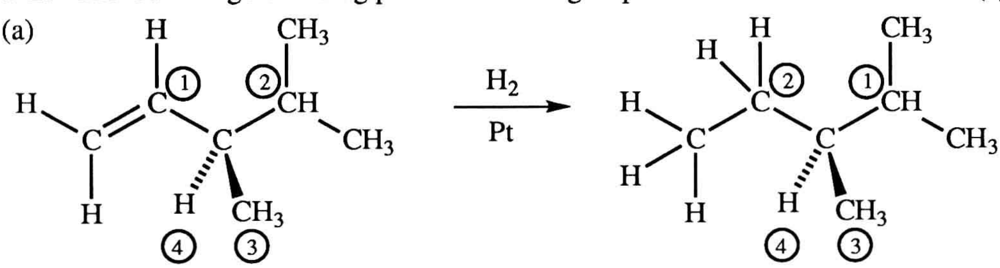
(b) 

racemization

(c) 

retention of configuration

5-25 The Cahn-Ingold-Prelog priorities of the groups are the circled numbers in (a).

(a) 

(*R*)-3,4-dimethyl-1-pentene (*S*)-2,3-dimethylpentane

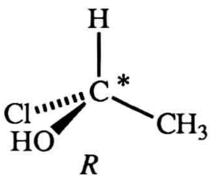
(b) The reaction did not occur at the chiral center, so the configuration of the chiral center has not changed—the reaction went with retention. What did change was the priority of the groups in the *R*,*S* system of nomenclature, which resulted in a change of *designation* of configuration. The designations *R* and *S* cannot be used *without thought* to determine whether configuration has changed in a reaction.

(c) There is no general correlation between *R* and *S* designation and the physical property of optical rotation. Professor Wade's poetic couplet makes an important point: do not confuse an object and its properties with the name for that object. (Scholars of Shakespeare have come to believe that this quote from Juliet is a veiled reference to designation of *R*,*S* configuration versus optical rotation of a chiral molecule.)

5-26 Refer to the Glossary and the text for definitions and examples.

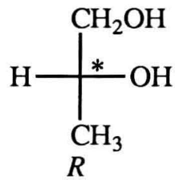
5-27

(a)



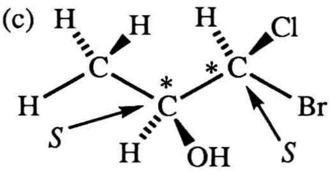
chiral

(b)



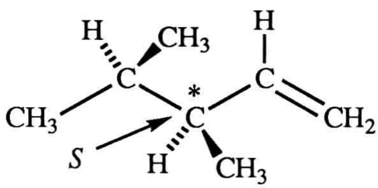
chiral

(c)



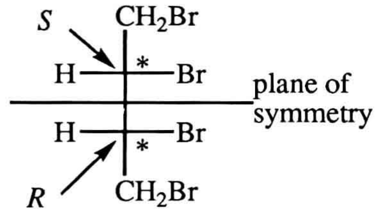
chiral

(d)



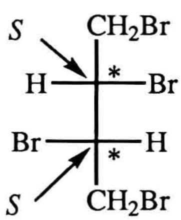
chiral

(e)



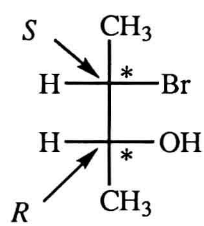
meso; achiral

(f)



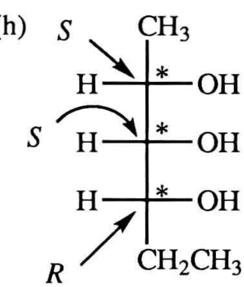
chiral

(g)



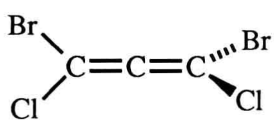
chiral

(h)



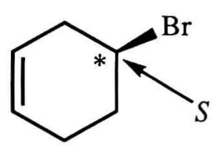
chiral

(i)



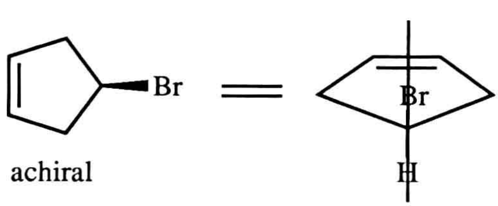
chiral molecule, but no chiral centers

(j)



chiral

(k)

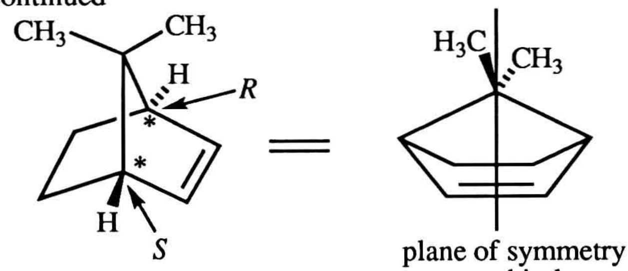


achiral

plane of symmetry

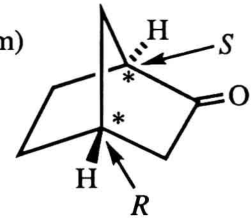
5-27 continued

(l)



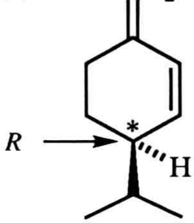
plane of symmetry
meso; achiral

(m)



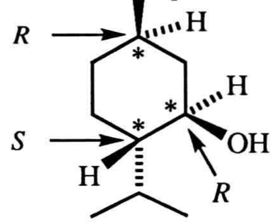
chiral

(n)



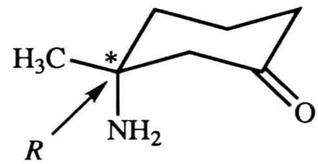
chiral

(o)



chiral

(p)

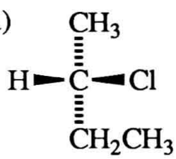


(NH_2 is group 1,
CH_3 is group 4)

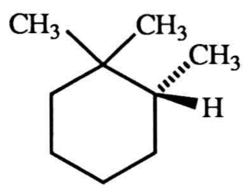
chiral

5-28

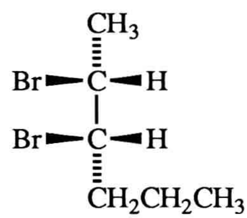
(a)



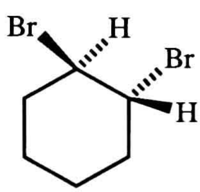
(b)



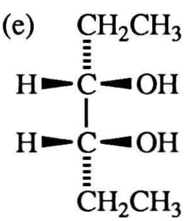
(c)



(d)

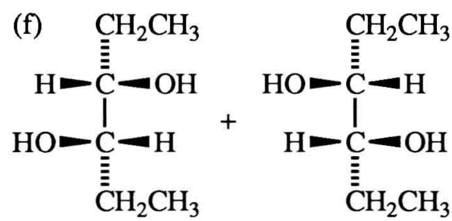


(e)



meso

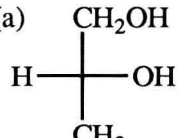
(f)



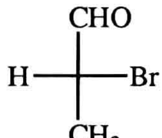
racemic mixture

5-29

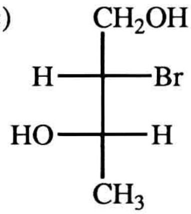
(a)



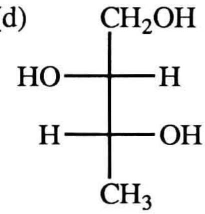
(b)



(c)

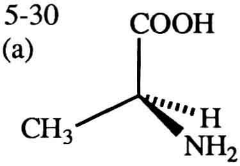


(d)

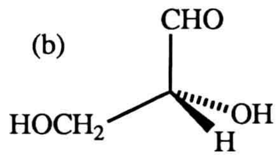


5-30

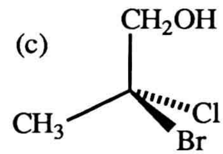
(a)



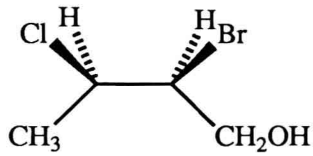
(b)



(c)



(d)

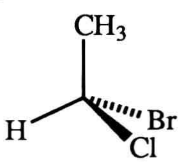


5-31

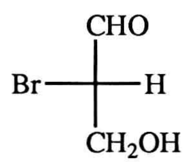
(a) same (meso)
(b) enantiomers
(c) enantiomers
(d) enantiomers
(e) enantiomers
(f) diastereomers
(g) enantiomers
(h) same compound

5-32

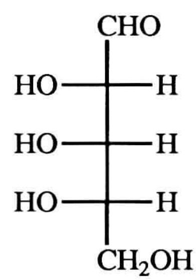
(a)



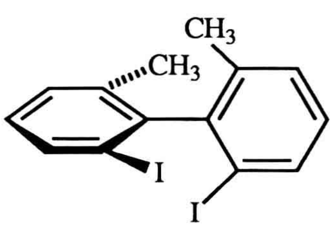
(b)



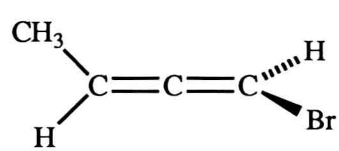
(c)



(d)

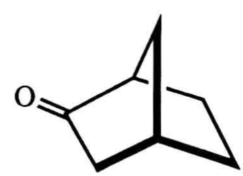


(e)

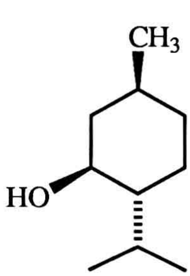


(f) plane of symmetry—no enantiomer

(g)



(h)



(i)