

Organic Chemistry

Fourth Edition

ROBERT THORNTON MORRISON

ROBERT NEILSON BOYD

New York University

Allyn and Bacon, Inc.

Boston, London, Sydney, Toronto

Production supervisor: Judith Fiske
Production editor: Mary Hill
Cover designers: Vicky Prescott
Christy Rosso

1973, 1966, 1959 by Allyn and Bacon,
Newton, Massachusetts 02159. All
part of the material protected by this
may be reproduced or utilized in any form
electronic or mechanical, including
photocopying, recording, or by any information storage and
retrieval system, without written permission from the

Indexing in Publication Data

tion

3

ic. I. Boyd, Robert Neilson.

547 82-8855

Photograph: 18-Crown-6.

United States of America.
3 2 1 87 86 85 84 83 82

Stereochemistry

4.1 Stereochemistry and stereoisomerism

The science of organic chemistry, we said, is based on the relationship between molecular structure and properties. That part of the science which deals with structure *in three dimensions* is called **stereochemistry** (Gr.: *stereos*, solid).

One aspect of stereochemistry is *stereoisomerism*. Isomers, we recall, are different compounds that have the same molecular formula. The particular kind of isomers that are different from each other *only* in the way the atoms are oriented in space (but are like one another with respect to which atoms are joined to which other atoms) are called **stereoisomers**.

Pairs of stereoisomers exist that differ so little in structure—and hence in properties—that of all the physical measurements we can make, only one, involving a special instrument and an unusual kind of light, can distinguish between them. Yet, despite this close similarity, the existence of such stereoisomers provides us with one of our most sensitive probes into mechanisms of chemical reactions; very often, one of these isomers is selected for study, not because it is different from ordinary compounds in its three-dimensional chemistry, but because it can be made to reveal what ordinary compounds hide. And, again despite their close similarity, one isomer of such a pair may serve as a nourishing food, or as an antibiotic, or as a powerful heart stimulant, and the other isomer may be useless.

We have already (Secs. 3.3 and 3.5) begun our study of the branch of stereochemistry called *conformational analysis*. In this chapter we shall, first, learn how to predict the existence of the kinds of stereoisomers called *enantiomers* and *diastereomers*, how to represent and designate their structures, and, in a general way, how their properties will compare. Then, in the latter part of the chapter, the emphasis will shift from what these isomers *are* to how they are formed, what they do, and what they can tell us. But stereochemistry permeates organic chemistry, and we shall return to it again and again throughout the rest of the book: to add to our knowledge of the fundamental concepts of stereochemistry; and simply to use it to help us understand what is going on in chemical reactions.

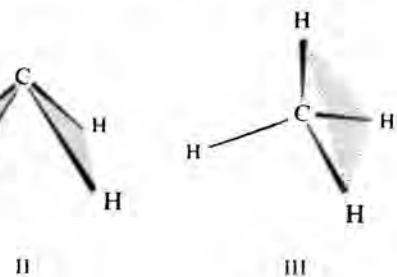
the methane molecule can be applied to the molecules.

on, x-ray diffraction, and spectroscopy shows whether atoms its bonds are directed toward the s 1874, years before the direct determination the tetrahedral carbon atom was proposed by student at the University of Utrecht) and, proposal was based upon the evidence of **isomer**

ance of formula CH_3Y has ever been found. e compound of formula CH_3Cl ; bromination CH_3Br . Similarly, only one CH_3F is known, holds true if Y represents, not just an atom, up is so complicated that in itself it brings CH_3OH , only one CH_3COOH , only one

arrangement of atoms in methane? It suggests is equivalent to every other hydrogen atom, them gives rise to the same product. If the equivalent, then replacement of one would cement of another, and isomeric substitution

methane be arranged so that the four hydrogen such arrangements: (a) a *planar* arrangement a rectangle (or square) and a hydrogen atom



ngement (II) in which carbon is at the apex is at each corner of a square base; (c) a carbon is at the center of a tetrahedron and

ese arrangements could give rise to only one ys for problems like this, the answer lies in rops and toothpicks can be used to make ond angles of ordinary molecular models are wo identical models of I. In one model we

models are superimposable, they simply represent two molecules of the same compound; if the models are not superimposable, they represent molecules of different compounds which, since they have the same molecular formula, are by definition *isomers* (p. 40). Whichever hydrogen we replace in I (or in II or III), we get the same structure. From any arrangement other than these three, we would get more than one structure.

As far as compounds of the formula CH_3Y are concerned, the evidence of isomer number limits the structure of methane to one of these three possibilities.

Problem 4.1 How many isomers of formula CH_3Y would be possible if methane were a pyramid with a *rectangular* base? What are they? (*Hint*: If you have trouble with this question now, try it again after you have studied Sec. 4.7.)

For any atom Y and for any atom Z, only one substance of formula CH_2YZ has ever been found. Halogenation of methane, for example, yields only one compound of formula CH_2Cl_2 , only one compound of formula CH_2Br_2 , and only one compound of formula CH_2ClBr .

Of the three possible structures of methane, only the tetrahedral one is consistent with this evidence.

Problem 4.2 How many isomers of formula CH_2YZ would be expected from each of the following structures for methane? (a) Structure I with carbon at the center of a rectangle; (b) structure I with carbon at the center of a square; (c) structure II; (d) structure III.

Thus, only the tetrahedral structure for methane agrees with the evidence of isomer number. It is true that this is negative evidence; one might argue that isomers exist which have never been isolated or detected simply because the experimental techniques are not good enough. But, as we said before, any compound that contains carbon bonded to four other atoms can be considered to be a derivative of methane; in the preparation of hundreds of thousands of compounds of this sort, the number of isomers obtained has always been consistent with the concept of the tetrahedral carbon atom.

There is additional, positive evidence for the tetrahedral carbon atom: the finding of just the kind of isomers—*enantiomers*—that are predicted for compounds of formula CWXYZ . It was the existence of enantiomers that convinced van't Hoff and LeBel that the carbon atom is tetrahedral. But to understand what enantiomers are, we must first learn about the property called *optical activity*.

4.3 Optical activity. Plane-polarized light

Light possesses certain properties that are best understood by considering it to be a wave phenomenon in which the vibrations occur at right angles to the direction in which the light travels. There are an infinite number of planes passing through the line of propagation, and ordinary light is vibrating in all these planes.

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.