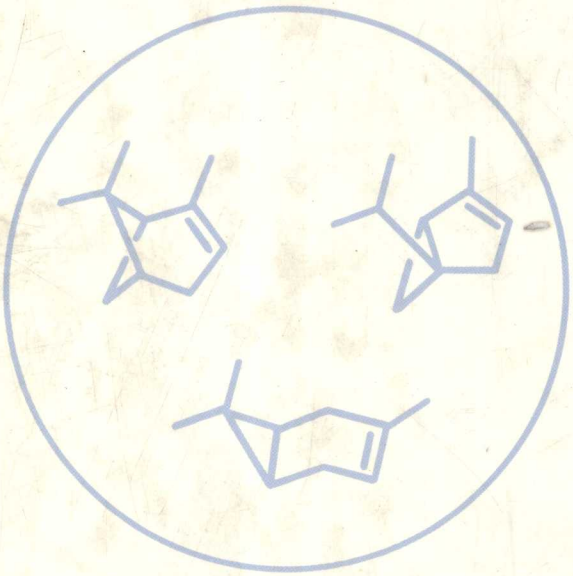
Studies in Organic Chemistry—EDITOR: Paul G. Gassman Volume 1

# chemistry of the monoterpenes

## an encyclopedic handbook

## part B



WILLIAM F. ERMAN

# Chemistry of the Monoterpenes

## An Encyclopedic Handbook

Part B

**WILLIAM F. ERMAN**
Miami Valley Laboratories
The Procter & Gamble Company
Cincinnati, Ohio


MARCEL DEKKER, INC. New York • Basel

**Library of Congress Cataloging in Publication Data**

Erman, William F., [date]
Chemistry of the monoterpenes.

(Studies in organic chemistry ; v. 11)
Includes bibliographies and index.
1. Monoterpenes. I. Title II. Series.
QD416.E75 1985 547.7'1 85-4528
ISBN 0-8247-1573-X (pt. A)
ISBN 0-8247-7312-8 (pt. B)



MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

# Preface

A new acquaintance on learning about my interest in terpene chemistry remarked that this area of chemistry seemed like a rather narrow field in which to conduct research. When I relayed this comment to my colleagues, they were predictably amused, for their explorations in terpene chemistry had led them into several disciplines of chemistry--organic, physical, analytical, and biological--and into a variety of intriguing fields where terpenes have been utilized--e.g., flavors, perfumes, insecticides, herbicides, and pharmaceuticals.

Terpene chemistry offers the chemist a variety of challenges: (1) isolation, structure elucidation, and determination of the absolute configuration of a group of exotically constructed natural products utilizing a multitude of analytical separation techniques, numerous spectral tools, and X-ray crystallography; (2) in vitro and in vivo tracer studies for the purpose of elucidating the often complex biogenetic pathways of these compounds; (3) intricate stereochemical problems including the effects of stereochemistry on the course of organic reactions; (4) a multitude of complex synthetic objectives; (5) the unraveling of the mechanisms of bizarre rearrangement reactions; and (6) a study of carbonium ion, carbanion, carbene, free radical, and concerted processes which may be acid-catalyzed, base-catalyzed, thermally induced, or photoinitiated and may involve oxidation, reduction, displacement, elimination and addition reactions, to name a few. Far from being narrow and limited, terpene chemistry includes almost all of the attractive aspects of organic and analytical chemistry.

Of the various classifications of terpenes--monoterpenes, sesquiterpenes, and the higher terpenes--the chemistry of the first class is perhaps the most interesting. Monoterpenes are more abundant in nature and are more easily synthesized in commercial quantities; therefore they are more readily available for

chemical studies. With a few exceptions, the sesqui- and higher terpenes have been isolated or synthesized only in small quantities; consequently, fewer chemical studies have been conducted on these terpenes.

The treatment of monoterpene chemistry in this treatise is not intended to be comprehensive. We have attempted to familiarize the reader with the most common monoterpene structural types encountered in nature, their biogenetic pathways, the nomenclature of the principal monoterpene skeletons, the reactions and techniques used to delineate the structures of some of the more common monoterpenes, the important stereochemical features of the terpene structures including their absolute configurations, and some of the general and/or most interesting synthetic approaches to the monoterpenes. However, in most instances we have placed greatest emphasis on chemical reactions of the monoterpenes. There are some exceptions. Like the sesqui- and higher terpenes, the geminate dimethylcyclohexanes (Chapter 5), the cyclopentanes (Chapter 6), and the monoterpene phenols (Chapter 12) have been isolated or synthesized only in small quantities, and, consequently, few studies of the chemical behavior of these classes of monoterpenes have been conducted. For this reason, the primary emphasis in these chapters (5, 6, 12) is on structure elaboration and synthesis.

A discussion of chemical reactions is incomplete without inclusion of some information about reaction mechanisms. Because of the speculative and controversial nature of many of the reaction pathways described here and the rapid rate at which ideas about the mechanisms of certain of these reactions are changing, the mechanistic hypotheses presented here are tentative. Nonetheless, we hope that the mechanistic reasoning offered here will clarify the otherwise nondescript chemical behavior of some of the monoterpenes.

Very little information about the spectral parameters and physical properties of the monoterpenes has been discussed here. Such data are described in a handbook by T. K. Devon and A. I. Scott (Handbook of Naturally Occurring Compounds, Vol. II, Terpenes, Academic Press, New York, 1972) and a handbook by S. Dev, J. S. Yadav, and A. Narula (Handbook of Terpenoids, Monoterpenoids, CRC Press, Inc., Boca Raton, Florida, 1982).

Special thanks are due to Dr. Paul Gassman, who read and critiqued the entire manuscript and suggested many excellent revisions. I am grateful to Charlotte Hutfles, Jacoba Atkins, Olga Carman, Barbara Beimesch and Rose Blanchet for reading and making corrections on portions of the manuscript. I particularly want to acknowledge those who typed and drew the structures for the several revisions of the manuscript--Beverly Nixon, Lucille Walsh, Loretta Hallbach, Charlene Wood, Mona Moore, Beverly Perkins, Jean Gullion, Ruth

Frankenstein, Rosemary Schlensker, Peggy Sehlhorst, and Sandra Galligan--and to those who skillfully and painstakingly completed the artwork for the camera-ready manuscript: Carol Dixon, Lisa Erman, Rosanne Erman, and Eileen Fletcher. I am especially indebted to Lucille Walsh who typed and drew the structures for the original manuscript and typed most of the camera-ready manuscript, to Loretta Hallbach who typed an entire revision of the manuscript and Beverly Nixon who coordinated the extensive work on the camera-ready manuscript. I would also like to thank the editors of Marcel Dekker, Inc. for their guidance in preparing the manuscript.

Some acknowledgement is due to our dining room table which served as a desk for the writing of the entire manuscript. That poor table has been covered with journals, books, papers, articles, etc., and hasn't enjoyed a normal life of Sunday dinners for several years. Today, at last, it is covered with a beautiful tablecloth, plates and silverware and is ready for the author's dinner with the loving, patient and understanding family to whom these volumes are dedicated: my wife, Rosemary, and our four children--Timothy, Lisa, Rosanne and Michael.

William F. Erman

# Contents of Part B

# Contents of Part A