

The Chemistry of Dienes and Polyenes. Volume 1

Edited by Zvi Rappoport

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The chemistry of
dienes and polyenes

THE CHEMISTRY OF FUNCTIONAL GROUPS

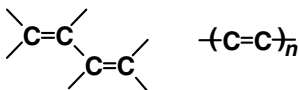
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 - Nitrones, nitronates and nitroxides
 - Crown ethers and analogs
 - Cyclopropane derived reactive intermediates
 - Synthesis of carboxylic acids, esters and their derivatives
 - The silicon–heteroatom bond
 - Syntheses of lactones and lactams
- The syntheses of sulphones, sulphoxides and cyclic sulphides

Patai's 1992 guide to the chemistry of functional groups—*Saul Patai*



The chemistry of **dienes and polyenes**

Volume 1

Edited by

ZVI RAPPOPORT

The Hebrew University, Jerusalem

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To

Judith and Zeev

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Foreword

In recent years *The Chemistry of Functional Groups* series has included three volumes on composite functional groups in which a C=C double bond was attached to another group. *The chemistry of enones* (edited by S. Patai and Z. Rappoport) appeared in 1989; *The chemistry of enols* (edited by Z. Rappoport) appeared in 1990 and *The chemistry of enamines* (edited by Z. Rappoport) appeared in 1994. We believe that the time has arrived for a book dealing with the combination of C=C double bonds, namely dienes and polyenes. The two double bonds can be conjugated, and conjugated dienes have a chemistry of their own, but even non-conjugated dienes show certain reactions that involve both double bonds. Allenes and cumulenes, which represent a different combination of the double bonds were treated in *The chemistry of ketenes, allenes and related compounds*, edited by S. Patai in 1980.

The present volume contains 21 chapters written by experts from 11 countries and is the first volume of a set of two. We hope that the missing topics will be covered in the second volume which is planned to appear in 2–3 years' time.

The present volume deals with the properties of dienes, described in chapters on theory, structural chemistry, conformations, thermochemistry and acidity and in chapters dealing with UV and Raman spectra, with electronic effects and the chemistry of radical cations and cations derived from them. The synthesis of dienes and polyenes, and various reactions that they undergo with radicals, with oxidants, under electrochemical conditions, and their use in synthetic photochemistry are among the topics discussed. Systems such as radialenes, or the reactions of dienes under pressure, comprise special topics of these functional groups.

The literature coverage is up to 1995 or 1996.

I would be grateful to readers who call my attention to mistakes in the present volume.

Jerusalem
August, 1996

ZVI RAPPOPORT

The Chemistry of Functional Groups

Preface to the series

The series 'The Chemistry of Functional Groups' was originally planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the preparation, properties and reactions of the functional group treated and on the effects which it exerts both in the immediate vicinity of the group in question and in the whole molecule.

A voluntary restriction on the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series and in textbooks (i.e. in books which are usually found in the chemical libraries of most universities and research institutes), should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the topic. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

It is realized that no plan can be devised for a volume that would give a complete coverage of the field with no overlap between chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters. In this manner, sufficient freedom is given to the authors to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

- (a) An introductory chapter deals with the general and theoretical aspects of the group.
- (b) Chapters discuss the characterization and characteristics of the functional groups, i.e. qualitative and quantitative methods of determination including chemical and physical methods, MS, UV, IR, NMR, ESR and PES — as well as activating and directive effects exerted by the group, and its basicity, acidity and complex-forming ability.
- (c) One or more chapters deal with the formation of the functional group in question, either from other groups already present in the molecule or by introducing the new group directly or indirectly. This is usually followed by a description of the synthetic uses of the group, including its reactions, transformations and rearrangements.
- (d) Additional chapters deal with special topics such as electrochemistry, photochemistry, radiation chemistry, thermochemistry, syntheses and uses of isotopically labelled compounds, as well as with biochemistry, pharmacology and toxicology. Whenever applicable, unique chapters relevant only to single functional groups are also included (e.g. 'Polyethers', 'Tetraaminoethylenes' or 'Siloxanes').

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the authors and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, some volumes may be published without giving consideration to the originally planned logical order of the chapters.

Since the beginning of the Series in 1964, two main developments have occurred. The first of these is the publication of supplementary volumes which contain material relating to several kindred functional groups (Supplements A, B, C, D, E, F and S). The second ramification is the publication of a series of 'Updates', which contain in each volume selected and related chapters, reprinted in the original form in which they were published, together with an extensive updating of the subjects, if possible, by the authors of the original chapters. A complete list of all above mentioned volumes published to date will be found on the page opposite the inner title page of this book. Unfortunately, the publication of the 'Updates' has been discontinued for economic reasons.

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editors.

The publication of this series would never have been started, let alone continued, without the support of many persons in Israel and overseas, including colleagues, friends and family. The efficient and patient co-operation of staff-members of the publisher also rendered us invaluable aid. Our sincere thanks are due to all of them.

The Hebrew University
Jerusalem, Israel

SAUL PATAI
ZVI RAPPOPORT

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List of abbreviations used

Ac	acetyl (MeCO)
acac	acetylacetone
Ad	adamantyl
AIBN	azoisobutyronitrile
Alk	alkyl
All	allyl
An	anisyl
Ar	aryl
Bz	benzoyl (C ₆ H ₅ CO)
Bu	butyl (also <i>t</i> -Bu or Bu ^{<i>t</i>})
CD	circular dichroism
CI	chemical ionization
CIDNP	chemically induced dynamic nuclear polarization
CNDO	complete neglect of differential overlap
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAH	diisobutylaluminium hydride
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulphoxide
ee	enantiomeric excess
EI	electron impact
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance
Et	ethyl
eV	electron volt

Fc	ferrocenyl
FD	field desorption
FI	field ionization
FT	Fourier transform
Fu	furyl(OC_4H_3)
GLC	gas liquid chromatography
Hex	hexyl(C_6H_{13})
<i>c</i> -Hex	cyclohexyl(C_6H_{11})
HMPA	hexamethylphosphortriamide
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
<i>i</i> -	iso
Ip	ionization potential
IR	infrared
ICR	ion cyclotron resonance
LAH	lithium aluminium hydride
LCAO	linear combination of atomic orbitals
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M	metal
<i>M</i>	parent molecule
MCPBA	<i>m</i> -chloroperbenzoic acid
Me	methyl
MNDO	modified neglect of diatomic overlap
MS	mass spectrum
<i>n</i>	normal
Naph	naphthyl
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
NMR	nuclear magnetic resonance
Pc	phthalocyanine
Pen	pentyl(C_5H_{11})
Pip	piperidyl($\text{C}_5\text{H}_{10}\text{N}$)
Ph	phenyl
ppm	parts per million
Pr	propyl (also <i>i</i> -Pr or Pr^i)
PTC	phase transfer catalysis or phase transfer conditions
Pyr	pyridyl ($\text{C}_5\text{H}_4\text{N}$)

R	any radical
RT	room temperature
<i>s</i> -	secondary
SET	single electron transfer
SOMO	singly occupied molecular orbital
<i>t</i> -	tertiary
TCNE	tetracyanoethylene
TFA	trifluoroacetic acid
THF	tetrahydrofuran
Thi	thienyl(SC_4H_3)
TLC	thin layer chromatography
TMEDA	tetramethylethylene diamine
TMS	trimethylsilyl or tetramethylsilane
Tol	tolyl(MeC_6H_4)
Tos or Ts	tosyl(<i>p</i> -toluenesulphonyl)
Trityl	triphenylmethyl(Ph_3C)
Xyl	xylyl($\text{Me}_2\text{C}_6\text{H}_3$)

In addition, entries in the 'List of Radical Names' in *IUPAC Nomenclature of Organic Chemistry*, 1979 Edition. Pergamon Press, Oxford, 1979, p. 305–322, will also be used in their unabbreviated forms, both in the text and in formulae instead of explicitly drawn structures.