

*The Chemistry of Dienes and Polyenes. Volume 2*

Edited by Zvi Rappoport

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The chemistry of  
**dienes and polyenes**

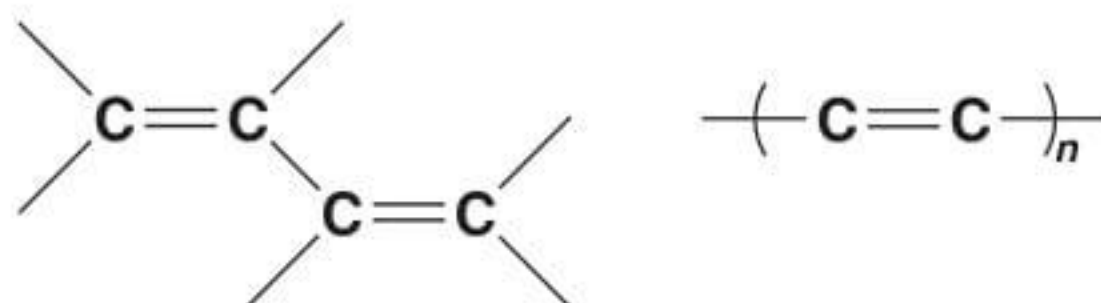
## THE CHEMISTRY OF FUNCTIONAL GROUPS

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- The chemistry of  $\alpha$ -haloketones,  $\alpha$ -haloaldehydes and  $\alpha$ -haloimines
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    - The silicon–heteroatom bond
    - Synthesis of lactones and lactams
  - Syntheses of sulphones, sulphoxides and cyclic sulphides
- Patai's 1992 guide to the chemistry of functional groups — *Saul Patai*



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# The chemistry of **dienes and polyenes**

Volume 2

*Edited by*

ZVI RAPPOPORT

*The Hebrew University, Jerusalem*

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To  
**Ron Johnson**  
and  
the late  
**Nir Poraz**

*To give and not to take*

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# Foreword

The first volume on *The Chemistry of Dienes and Polyenes* in the series 'The Chemistry of Functional Groups' (edited by Z. Rappoport) was published in 1997 and included 21 chapters—its table of contents appears at the end of this volume following the indexes. It was recognized then that several topics were not covered and a promise was made that a second volume covering these topics would be published in a few years.

The present volume contains 13 chapters written by experts from 11 countries, and treats topics that were not covered, or that are complementary to topics covered in Volume 1. They include chapters on mass spectra and NMR, two chapters on photochemistry complementing an earlier chapter on synthetic application of the photochemistry of dienes and polyenes. Two chapters deal with intermolecular cyclization and with cycloadditions, and complement a chapter in Volume 1 on intramolecular cyclization, while the chapter on reactions of dienes in water and hydrogen-bonding environments deals partially with cycloaddition in unusual media and complements the earlier chapter on reactions under pressure. The chapters on nucleophilic and electrophilic additions complements the earlier chapter on radical addition. The chapter on reduction complements the earlier ones on oxidation. Chapters on organometallic complexes, synthetic applications and rearrangement of dienes and polyenes are additional topics discussed.

The literature coverage is up to the end of 1998 or early 1999.

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

Jerusalem  
January 2000

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

Sadly, Saul Patai who founded 'The Chemistry of Functional Groups' series died in 1998, just after we started to work on the 100th volume of the series. As a long-term collaborator and co-editor of many volumes of the series, I undertook the editorship and this is the second volume to be edited since Saul Patai passed away. I plan to continue editing the series along the same lines that served for the first hundred volumes and I hope that the continuing series will be a living memorial to its founder.

The Hebrew University  
Jerusalem, Israel  
May 2000

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  |
|        |   |
| Bn     | benzyl  |
| Bz     | benzoyl (C <sub>6</sub> H <sub>5</sub> CO)      |
| Bu     | butyl (also <i>t</i> -Bu or Bu <sup>t</sup> )   |
|        |   |
| CD     | circular dichroism                              |
| CI     | chemical ionization                             |
| CIDNP  | chemically induced dynamic nuclear polarization |
| Cp     | $\eta^5$ -cyclopentadienyl                      |
| Cp*    | $\eta^5$ -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              |
| DIBALH | 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( $\text{OC}_4\text{H}_3$ )               |
| GLC           | gas liquid chromatography                      |
| Hex           | hexyl( $\text{C}_6\text{H}_{13}$ )             |
| <i>c</i> -Hex | cyclohexyl( $\text{C}_6\text{H}_{11}$ )        |
| 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   |
| 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( $\text{C}_5\text{H}_{11}$ )            |
| Pip           | piperidyl( $\text{C}_5\text{H}_{10}\text{N}$ ) |
| Ph            | phenyl   |
| ppm           | parts per million                              |
| Pr            | propyl (also <i>i</i> -Pr or $\text{Pr}^i$ )   |
| PTC           | phase transfer catalysis                       |
| 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 <sub>4</sub> H <sub>3</sub> )              |
| TLC        | thin layer chromatography                             |
| TMEDA      | tetramethylethylene diamine                           |
| TMS        | trimethylsilyl or tetramethylsilane                   |
| Tol        | tolyl(MeC <sub>6</sub> H <sub>4</sub> )               |
| Tos or Ts  | tosyl( <i>p</i> -toluenesulphonyl)                    |
| Trityl     | triphenylmethyl(Ph <sub>3</sub> C)                    |
|            |   |
| Xyl        | xylyl(Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) |

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.