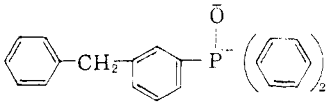
alkali metals utimately contain the same radical anion, different phosphorus-containing anions are formed. A solution of two moles of sodium per mole of triphenylphosphine oxide in 1,2-dimethoxyethane reacts with benzyl chloride forming benzyldiphenylphosphine oxide in 77% yield. The predominant portion of the cleaved phenyl group forms benzene. Methyldiphenyl- and ethyldiphenylphosphine oxides and tetramethylenebis-(diphenylphosphine oxide) were prepared similarly in 65, 62 and 66% yields by reaction with methyl iodide, ethyl bromide and tetramethylene bromide, respectively.

When, however, solutions of two moles of lithium or potassium per mole of triphenylphosphine oxide were treated with benzyl chloride, the only product isolated was a compound $C_{25}H_{21}PO$, m.p. 237–238°, formed in 20% yield. *Anal.* Calcd. for $C_{25}H_{21}PO$: C, 81.52; H, 5.71; P, 8.42; mol. wt., 368. Found: C, 80.81, 80.30; H, 6.17, 6.04; P, 8.01; mol. wt., 385. This compound has infrared absorption bands at 1185, 790 and 720 cm.$^{-1}$, indicating it to be a *m*-substituted tertiary phosphine oxide consistent with its formulation as diphenyl (α-phenyl-*m*-tolyl) phosphine oxide, I.



I

Reaction of benzyldiphenylphosphine oxide with sodium resulted in the formation of phosphine oxide "ylid,"[5] since reaction with ethyl bromide formed (α-ethylbenzyl)-diphenylphosphine oxide, m.p. 185–186° in 35% yield. *Anal.* Calcd. for $C_{21}H_{21}PO$: C, 78.73; H, 6.61; P, 9.67; mol. wt., 320. Found: C, 78.59; H, 6.90; P, 9.78; mol. wt., 330.

Ethyldiphenylphosphine oxide, however, after reaction with sodium and then benzyl chloride, formed benzylethylphenylphosphine oxide in 39% yield.

The phenyl cleavage of triphenylphosphine and triphenylphosphine oxide by sodium is consistent with the initial formation of a radical anion either adsorbed at the metal surface or in low concentration in solution which collapses to phenyl radical and phosphide or phosphinite anion. Phenyl radical may then dimerize or form phenide ion by oxidizing a second mole of sodium. This scheme is supported by the formation of phenyllithium during the cleavage of triphenylamine[1] and by the ease with which free radicals are reduced by alkali metals.[6]

The reaction of lithium or potassium with triphenylphosphine oxide, however, may involve ring metalation prior to reaction with halide as evidenced by the formation of I. Further experiments to clarify the behavior of these and related organophosphorus compounds are in progress.

[5] L. Horner, H. Hoffman and H. G. Wippel, *Ber.*, **91**, 61 (1958).

[6] H. E. Bent and N. B. Keevil, THIS JOURNAL, **58**, 1228 (1936).

AMERICAN CYANAMID COMPANY
CENTRAL RESEARCH DIVISION
STAMFORD LABORATORIES
STAMFORD, CONNECTICUT

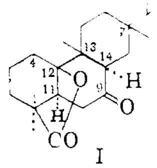
A. KENTARO HOFFMANN
A. G. TESCH

RECEIVED AUGUST 24, 1959

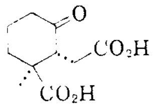
THE ABSOLUTE CONFIGURATION OF ROSENONOLACTONE AND RELATED DITERPENOIDS

Sir:

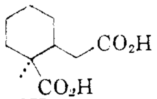
Evidence previously adduced[1,2] indicates that rosenonolactone, a diterpenoid metabolite of *Trichothecium roseum* Link, has the structure and *relative* stereochemical configuration (I), in which no configurational assignment was allocated to the substituents at C-7. We now wish to present evidence which conclusively establishes the *absolute* configuration of several diterpenoids of the rosenonolactone group, such stereochemical information being of crucial importance in defining the nature of the biogenetic precursor(s)[3] of these mold metabolites.



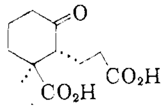
I



II



III



IV

A comparison of the optical rotatory dispersion curves[4] of (−)-*trans*-2-methyl-2-carboxy-6-ketocyclohexylacetic acid (II),[5] derived (after epimerization of the initially formed *cis*-acid) from ring A of rosenonolactone,[2,6] and of (−)-*trans*-2-methyl-2-carboxy-6-ketocyclohexylpropionic acid, the absolute configuration of which has been unequivocally established as (IV),[7] shows that both compounds exhibit a negative Cotton effect and that the rotatory dispersion curves are almost superimposable. The conformations of (II) and (IV) will be identical and hence the C_{10} acid derived from ring A has the absolute configuration (II).

Independent verification of this assignment was made by Clemmensen reduction of II, which provided (−)-*cis*-2-methyl-2-carboxycyclohexylacetic acid (III) of known absolute configuration.[8]

[1] B. Green, A. Harris, W. B. Whalley and H. Smith, *Chemistry and Industry*, 1369 (1958).

[2] A. Harris, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1799 (1958); B. Green and W. B. Whalley, *ibid.*, in press.

[3] See "Ciba Foundation Symposium on the Biosynthesis of Terpenes and Sterols," Churchill, London, 1959, pp. 239–242 (by D. Arigoni), and pp. 258–260 (by A. J. Birch and H. Smith).

[4] For introduction to this approach see C. Djerassi, *Bull. Soc. Chim. France*, 741 (1957); C. Djerassi "Optical Rotatory Dispersion. Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter 10.

[5] The structure of the acid II has now been confirmed by synthesis of its racemate: alkylation of Hagemann's ester with ethyl chloroacetate, then alkaline cleavage furnished 2-methyl-6-ketocyclohex-1-ene acetic acid: addition of cyanide and alkaline saponification provided *d,l*-II.

[6] A. Robertson, W. R. Smithies and E. Tittensor, *J. Chem. Soc.*, 879 (1949).

[7] H. Inhoffen, S. Schütz, P. Rossberg, O. Berges, K.-H. Nordsiek, H. Plenio and E. Höroldt, *Ber.*, **91**, 2626 (1958).

[8] F. Gautschi, O. Jeger, V. Prelog and R. B. Woodward, *Helv. Chim. Acta*, **38**, 296 (1955).

Coupled with earlier evidence[1,2] on the relative configuration, the above results establish conclusively the absolute configuration of rosenonolactone (I) at positions 1, 11, 12, 13 and 14, iso-rosenonolactone being the 14β-isomer.[1] Our stereochemical conclusions also apply to a new metabolite (m.p. 115–116°, $[\alpha]_D$ +57° (Chl)) of *T. roseum*—9-deoxorosenonolactone—since its dihydro derivative proved to be identical with the desulfurization product of rosenonolactone 9-ethylene mercaptal. Finally, rosololactone[9] must possess the identical absolute configuration at C-1, C-12 and C-13 as rosenonolactone (I).

We are indebted to Prof. H. H. Inhoffen for speciments of (−)- and (+)-*trans*-2-methyl-2-carboxy-6-ketocyclohexylpropionic acid.

DEPARTMENTS OF CHEMISTRY
UNIVERSITY OF LIVERPOOL
LIVERPOOL, ENGLAND
EIDGENOSSISCHE TECHNISCHE HOCHSCHULE
ZURICH, SWITZERLAND
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

W. B. WHALLEY
B. GREEN
D. ARIGONI
J. J. BRITT
CARL DJERASSI

RECEIVED SEPTEMBER 9, 1959

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[9] A. Harris, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1807 (1958).

BOOK REVIEWS

Basic Physics of Atoms and Molecules. By U. FANO and L. FANO, Physicists, National Bureau of Standards. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N.Y. 1959. xv + 414 pp. 15.5 × 23.5 cm. Price, $10.00.

This book is concerned with the principles of atomic and molecular structure, and is featured as "quantum physics presented through analysis of experiments, requiring a minimum knowledge of physics and mathematics." The authors begin with a relatively elementary discussion of initial evidence for the existence of atoms, followed by a description of the methods of detection of atomic events, the Rutherford alpha scattering experiment, evidence for energy levels of atoms and radiation, leading to the essential features of atomic structure.

The next few chapters develop an approach to quantum theory and quantum mechanics through a survey of the properties of electromagnetic radiation and analysis of the behavior of radiation and particle beams. To illustrate basic concepts considerable use is made of the Stern–Gerlach experiment and the polarization of light. A discussion of the size of atoms and the uncertainty principle is followed by formulation of Schroedinger's equation. The stationary states of the hydrogen atom are developed and the properties associated with these states described. Effects of current circulation within the atom and evidence for electron spin are considered. Part 1 (basic concepts, total of 264 pp.) concludes with chapters on magnetic interactions and the Pauli exclusion principle.

Part 2, entitled "Aggregates of Particles" (70 pp.), begins with a discussion of atoms with many electrons, the independent electron approximation, shell structure and the periodic system. The nature of the chemical bond in simple molecules is discussed in some detail, including reference to both the atomic orbital and molecular orbital approximations. The shape of polyatomic molecules, multiple bonds, non-localized bonds, conjugate systems and metallic systems are considered briefly and qualitatively. This section concludes with an outline of the features of macroscopic aggregates.

A series of appendices (total 64 pp.) is included at the end of the book to provide a more detailed mathematical treatment of the interaction of particles, Fourier analysis, statistical methods, complex numbers, matrices and resonance theory. A small number of exercises are provided at the end of each chapter of Part 1 (*ca.* 48 for the entire book). Answers are provided. References to original research papers are not included.

The authors state that their book is directed primarily to research workers in the natural sciences and presupposes only a general knowledge of physics and mathematics. They intend only to give a qualitative picture of the properties of atoms and molecules rather than to teach how to calculate the solutions of quantum mechanical problems. The book is clearly written, follows a logical sequence of developments, and makes a valuable contribution toward the goal set by the authors. Those concerned with an introductory course dealing with the topics covered will certainly want to examine it carefully.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

N. W. GREGORY

Gas-Chromatographie. By A. I. M. KEULEMANS, Koninklijke/Shell-Laboratorium, Amsterdam. Englische Originalausgabe unter Mitarbeit von C. G. VERVER. Deutsche Ausgabe, mitbearbeitet und ubersetzt von E. CREMER, Vorstand des Physikalisch-Chemischen Institutes an der Universität Innsbruck. Verlag Chemie, Gm.b.H., Weinheim/Bergstr., Germany. 1959. xvi + 208 pp. 17 × 24.5 cm. Price, DM 24.—

The outstanding book "Gas Chromatography" by Dr. Keulemans, originally published in 1957, has now been revised and printed in a German edition. The structure and content of the original volume have been left intact. The first three chapters deal with the general aspects of chromatography, analytical applications of gas—liquid chromatography and the apparatus used in practice. The next three chapters discuss the theory of chromatographic separations with studies involving the mobile phase, stationary phase and the solid support. Special applications of gas–liquid and gas–solid chromatography are presented in the last two chapters.

Frau Prof. Erika Cremer in her translation and editing has improved on the original work by incorporating a subject index. Fifty-one additional references have been added which include papers presented at the Symposium on Gas Chromatography at Amsterdam in May, 1958. The chapter on gas–solid chromatography has been enlarged with notes on the separation of inert gases, resolution of isotopes, determination of free energies of adsorption and catalyst studies. The subject of adsorption chromatography has been added in the appendix replacing the original appendix on katharometers.

In an expanding field such as gas chromatography, this edition should continue to be of considerable value to those interested in the subject.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HOUSTON
HOUSTON 4, TEXAS

ALBERT ZLATKIS