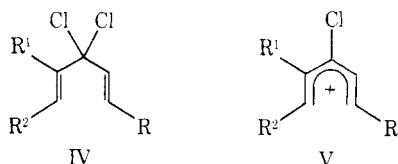


bromic acid at 100° for 2 hr, followed by work-up, gave 3,5-dimethyl-2-cyclopentenone¹⁰ in 83% yield. In a similar manner IIb was converted to 2-methyl-2-cyclopentenone (IIIb)¹¹ in 44% yield. When IIc was exposed to this acidic condition, the resulting product proved to be 3-butyl-2-methyl-2-cyclopentenone (IIIc)^{7,12} (56% yield), and none of the corresponding position isomer, 2-amyl-2-cyclopentenone, was detected. It should be noted that the original methyl group is not incorporated into the five membered ring and a long alkyl side chain resides at the 3-position. Accordingly dihydroisojasmone (IIId)¹² was obtained from II d (59% yield). Acid treatment of alcohol IIe resulted in the formation of 2-methyl-3-propenyl-2-cyclopentenone⁷ (70% yield). Under this acidic condition the anticipated isoallethronone (IIIe) isomerized to more thermodynamically stable conjugated dienone. Finally the sequence was used to prepare 2,3-decamethylene-2-cyclopentenone (III f), a versatile intermediate of pyridomuscone,¹³ muscone,¹⁴ and [10]metacyclophane synthesis.¹⁵ From 2-cyclododecylidene ethanol (If) the enone III f was obtained in 37% overall yield.

The mechanism of the cyclopentenone formation, which is not clear yet, can be rationalized by the following scheme. Conjugate dehydration of II gives IV,¹⁶ which easily ionizes to yield the pentadienyl cation V. Thermal conrotatory ring closure¹⁷ of V produces the cyclopentenyl cation. Deprotonation,¹⁶ followed by hydrolysis of the resulting chlorodiene, produces III.¹⁸



A typical experiment is illustrated by the preparation of dihydroisojasmone. To a solution of 3-methyl-2-nonenol (Id) (880 mg, 5.64 mmol) and cetyltrimethylammonium bromide (50 mg) in chloroform (3 ml), aqueous sodium hydroxide (1.5 g in 1.5 ml of water) was

(10) The primary product may be the isomer IIIa, which is, however, reported to isomerize to the obtained compounds under acidic conditions: I. N. Nazarov and A. N. Elizarova, *Otd. Khim. Nauk*, 295 (1951); *Chem. Abstr.*, 46, 914h (1952).

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(12) A. L. Voitsekhovskaya, N. A. Kosul'nikova, T. A. Rudol'fi, V. M. Dashunin, and V. N. Belov, *Zh. Vses. Khim. Obshchest.*, 10, 702 (1965); *Chem. Abstr.*, 64, 9588a (1966); A. L. Voitsekhovskaya, N. A. Kosul'nikova, T. A. Rudol'fi, R. I. Sharapova, V. M. Dashunin, and V. N. Belov, *Zh. Org. Khim.*, 3, 18 (1967); *Chem. Abstr.*, 66, 94712w (1967).

(13) K. Biemann, G. Büchi, and B. H. Walker, *J. Amer. Chem. Soc.*, 79, 5558 (1957).

(14) G. Ohloff, J. Becker, and K. H. Schulte-Elte, *Helv. Chim. Acta*, 50, 705 (1967); A. Eschenmoser, D. Felix, and G. Ohloff, *ibid.*, 50, 708 (1967); D. Felix, J. Schreiber, G. Ohloff, and A. Eschenmoser, *ibid.*, 54, 2896 (1971).

(15) S. Fujita, S. Hirano, and H. Nozaki, *Tetrahedron Lett.*, 403 (1972); S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, *Chem. Lett.*, 707 (1972).

(16) The olefin formation may be directed so that the more substituted olefin is formed.

(17) As to the cyclization of pentadienyl cation, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 58; P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, 91, 6404 (1969).

(18) When the reaction of cyclopropylcarbinols with acid was performed under more mild conditions (room temperature, shorter reaction time), dehydration occurred actually under negligible formation of cyclopentenones probably due to insufficient hydrolysis of the intermediates. Attempts to isolate and identify the observed nonpolar by-products have failed.

added in 15 min under a nitrogen atmosphere at 55°. After stirring for 3 hr the mixture was neutralized with dilute hydrochloric acid and then worked up. Distillation at 120–125° (5 mm) gave the adduct II d (806 mg, 60%). Successively alcohol II d (476 mg, 2 mmol) was mixed with 47% hydrobromic acid (3 ml) and heated at 100° for 9 hr. Work-up and tlc purification (silica gel, ether-hexane (3:1), $R_f = 0.7$) gave dihydroisojasmone (IIId) (196 mg, 59%), bp 130° (bath temperature) (3 mm).

The present simple procedure coupled with the selective dichlorocarbene addition possesses wide applicability. Extension of this reaction is being explored.

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Structure of Bacteriochlorophyll b¹

Sir:

Bacteriochlorophyll b (Bchl b)² is the principal green pigment of the photosynthetic bacterium *Rhodospseudomonas viridis*.³ The electron excitation spectrum of Bchl b is similar to but even more strongly red shifted than that of the bacteriochlorophyll a (Bchl a), **1**. It enables this bacterium to use light down to 9800 cm⁻¹ (1020 nm), the least energetic light used by any known photosynthetic organism. The close structural relationship between Bchl a and b was established by Brockmann and Kleber,⁴ who converted both to 2-desvinyl-2-acetylpyromethylpheophorbide a⁵ and established Mg as the central metal and phytol as the esterifying alcohol. The most distinct difference between Bchl a and b is the easy conversion of the latter into products related to chlorophyll a (Chl a), which corresponds formally to oxidation of the macrocycle from the tetrahydro- to the dihydroporphyrin level. As cis chlorins are easily oxidized to porphyrins and show a red-shifted visible absorption spectrum compared to the corresponding trans epimers,⁶ Brockmann⁴ in 1970 formulated Bchl b as the 3,4-cis epimer of Bchl a (structure 2).

At the end of the same year, Baumgarten⁷ proposed structure **3** for Bchl b, which formulates Bchl b as the Δ4,4a isomer of Chl a. The red shift in the electron excitation spectrum is explained by the α,β unsaturation of the Bchl a chromophore,⁸ and the easy "oxida-

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Eimhjellen, O. Aasmundrud, and A. Jensen, *Biochem. Biophys. Res. Commun.*, 10, 232 (1963).

(3) G. Drews and P. Giesbrecht, *Arch. Mikrobiol.*, 53, 255 (1966); N. Pfennig and H. G. Trueper, *Int. J. Syst. Bacteriol.*, 21, 19 (1971).

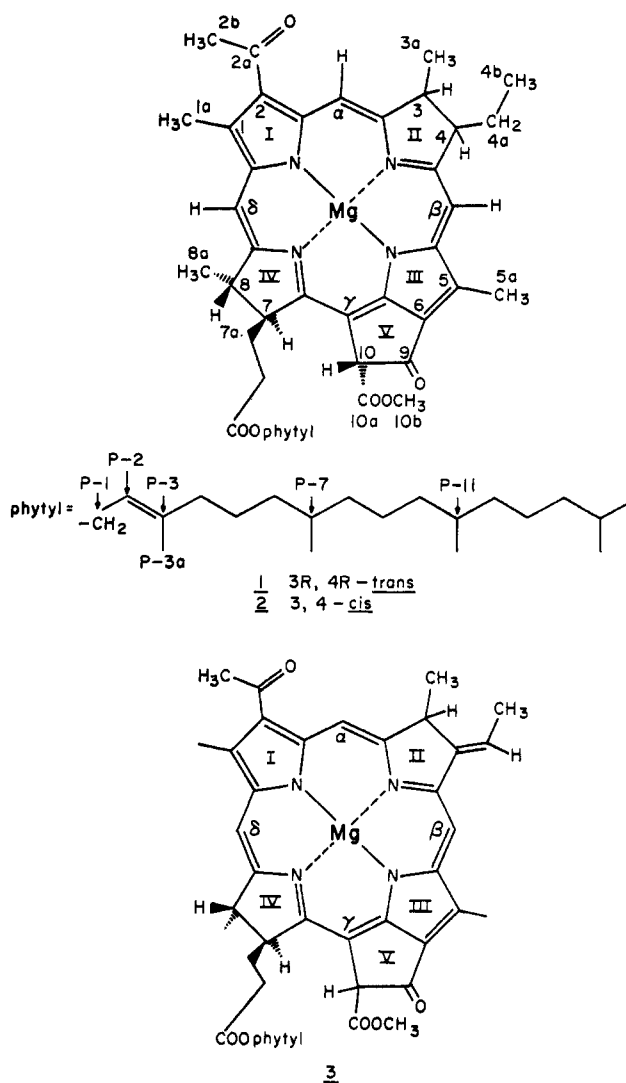
(4) H. Brockmann, Jr., and I. Kleber, *Tetrahedron Lett.*, 2195 (1970).

(5) H. H. Inhoffen, P. Jaeger, R. Maehlhof, and C. D. Mengler, *Justus Liebigs Ann. Chem.*, 704, 188 (1967).

(6) (a) H. H. Inhoffen, J. W. Buchler, and R. Thomas, *Tetrahedron Lett.*, 1145 (1969); (b) H. Wolf and H. Scheer, *Justus Liebigs Ann. Chem.*, 1710 (1973).

(7) D. L. Baumgarten, M.S. Thesis, Berkeley, 1970, UCRL-20242.

(8) In a similar manner, the Δ2,2a and Δ4,4a isomers of porphyrins exhibit a chlorin spectrum; cf. H. H. Inhoffen, H. Brockmann, Jr., and K. Bliesener, *Justus Liebigs Ann. Chem.*, 730, 173 (1969).



tion" to the Chl a level as an isomerization.⁹ While the evidence of Baumgarten⁷ against 2 was convincing, it was not sufficient to establish 3. We can now present ¹H nmr, mass spectral, and chemical evidence that strongly supports 3 as the structure of Bchl b.

Bchl b was extracted from *Rh. viridis* (ATCC No. 19567) and purified by the methods of Strain and Svec.¹⁰ Evidence for the validity of structure 3 for Bchl b is based on the following observations.

(a) The micro ozonolysis¹¹ of Bchl b, but not that of Chl a and Bchl a, yields acetaldehyde. The reaction was carried out in ethyl acetate (Baker, gc grade), and the acetaldehyde was identified by vpc (10 ft × 1/8 in., 5% DEGA on Chromosorb G at 22°, relative retention time vs. ethyl acetate = 0.16). Subsequent mass spectroscopy¹² (Biospect, Scientific Research Instruments (Baltimore) with chemical (CH₄) ionization and quadrupole analyzer) showed characteristic ions at *m/e* 59 (M + 15)⁺, 45 (M + 1)⁺, and 31 (CH₃O)⁺.

(9) The photosensitized conversion of Bchl b in acetone to a chlorin was already noticed by Eimhjellen.² For an acetone sensitized photoepimerization of tertiary carbon, cf. R. G. Salomon and J. K. Kochi, *Tetrahedron Lett.*, 4387 (1973).

(10) H. H. Strain and W. A. Svec, "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., pp 22-66.

(11) M. Beroza and B. A. Bierl, *Mikrochim. Acta*, 720 (1969).

(12) We are indebted to Dr. P. D. Klein and Dr. D. L. Hachey for the gcms measurements.

(b) The mass spectra (AEI MS 902 and Bendix TOF, direct inlet) of both bacteriopheophytins a and b (Bph a, b) show essentially the same fragmentation pattern, with the corresponding peaks in Bph b two mass units lower, however. Thus, Bph a has a molecular ion at *m/e* 888, Bph b at *m/e* 886. The characteristic fragment ions of Bph a at *m/e* 830, 592, 552, and 534 occur in Bph b at *m/e* 828, 590, 550, and 532, respectively. Both show an ion at *m/e* 278, thus confirming phytol as the esterifying alcohol in Bchl a¹³ and Bchl b.⁴

(c) The ¹H nmr spectrum (220-MHz pulse-Fourier transform-spectra, 10⁻² M in pyridine, spin-decoupling experiments in CW-CAT mode, all chemical shifts in δ (ppm) downfield from HMS) shows a doublet (3 protons, *J*₁ = 7 Hz) at δ 2.01 ppm, coupled to a double quartet (1 proton, *J*₁ = 7 Hz, *J*₂ = 2 Hz) at δ 6.84 ppm. The latter is coupled to a double quartet (1 proton, *J*₂ = 2 Hz, *J*₃ = 7 Hz) at δ 4.93 ppm, which in turn is coupled to a doublet (3 protons, *J*₃ = 7 Hz) at δ 1.66 ppm. In addition to this CH₃/CH/CH/CH₃-spin system, which we ascribe to the protons at positions 4b, 4a, 3, and 3a, respectively, all signals characteristic¹⁴ for ring IV and phytol, the meso and 10 protons as well as four isolated low-field methyl singlets (1a, 2b, 5a, 10b), are to be seen.

(d) Bchl b is oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in a fast two-electron oxidation,¹⁵ similar to Bchl a.¹⁶ The main product, however, is 2-desvinyl-2-acetyl-4-desethyl-4-(α-hydroxy)-ethylchlorophyll a, with at least three additional by-products. According to absorption spectra and tlc, none of these is 2-desvinyl-2-acetylchlorophyll a, which is obtained from Bchl a under the same conditions in 90% yield.¹⁶ The pheophytin of the 4-hydroxy compound was isolated by tlc on silica (CCl₄-acetone = 92:8, *R_F* = 0.2) in 30% overall yield: absorption spectrum (acetone) λ_{max} 678.5, 618, 542, 511, 414, 382 nm, relative intensities = 1:0.155:0.195:0.258:2.08:1.53; ¹H nmr spectrum (10⁻³ M in CDCl₃, 100 MHz PFT mode) 10.11, 10.08 ppm (1 H, split,¹⁷ β), 9.92 (s, α), 8.72 (s, δ), 6.24 (s, 10), 6.61 (q, *J* = 7 Hz, 1 H, 4a),¹⁸ 2.05 (d, *J* = 7 Hz, 3 H, 4b). In addition, all signals characteristic¹⁴ for ring IV and phytol as well as five low-field CH₃ singlets (1a, 2b, 3a, 5a, 10b) are observed.

In summary, all these findings are consistent with structure 3 and contradictory to structure 2. Bchl b may therefore be formulated as Δ4,4a-Bchl a. While the correlation of Brockmann⁴ implies for Bchl b the same 7*S*,8*S* configuration as for Chl a,¹⁹ the chiralities of the asymmetric C-3 and C-10, and the 4,4a double

(13) All comparative studies were performed with Bchl a from *Rhodospseudomonas palustris*, which contains phytol as the esterifying alcohol; cf. J. J. Katz, H. H. Strain, A. L. Harkness, M. H. Studier, W. A. Svec, T. R. Janson, and B. T. Cope, *J. Amer. Chem. Soc.*, **94**, 7938 (1972).

(14) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Amer. Chem. Soc.*, **85**, 3809 (1963).

(15) For a detailed investigation of the redox chemistry see J. J. Katz, H. Scheer, W. Svec, and B. Cope, to be submitted for publication.

(16) J. R. L. Smith and M. Calvin, *J. Amer. Chem. Soc.*, **88**, 4500 (1966).

(17) Similar splittings due to hindered rotation around the 2-2a bond are observed in a variety of 2a-hydroxy and alkoxy pheophorbides and pheoporphyryns; cf. Hugo Scheer, Ph.D. Thesis, Braunschweig, 1971.

(18) The 4a proton in the corresponding pyromethylpheophorbide a⁵ shows a chemical shift of δ 5.99 ppm.

(19) J. Fleming, *Nature (London)*, **216**, 151 (1967).

bond are unknown so far. It should be mentioned that Bchl b obviously provides a structural link between Bchl a and phycocyanobilin.²⁰ Both chromophores can be derived from Bchl b, the former by hydrogenation of the ethylidene group, the latter by oxidative fission of the macrocycle at the α -position.

(20) H. L. Crespi, *Biochemistry*, 7, 2232 (1968); A. Gossauer and W. Hirsch, *Tetrahedron Lett.*, 1451 (1973).

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Book Reviews*

The Origins of Life on the Earth. By STANLEY L. MILLER (University of California, San Diego) and LESLIE E. ORGEL (Salk Institute, La Jolla). Prentice-Hall Inc., Englewood Cliffs, N. J. 1973. x + 229 pp. \$10.95 (cloth); \$5.95 (paper).

The title of this book may not lead the reader to expect the amount of detailed chemistry that is in it, especially if he is a theologian or philosopher. The book is for undergraduate students in sciences who have had at least some organic chemistry, and preferably some physical chemistry as well, and for people in general whose background includes substantial knowledge of these subjects. There are orienting chapters on theories of the formation of the solar system and on historical geology, as well as a chapter on the possibilities of extraterrestrial life, but the bulk of the book deals in nearly undiluted form with chemistry, from prebiotic syntheses of simple molecules to biochemical evolution.

It is refreshing to have the authors admit in the very first sentence that "it must be admitted from the beginning that we do not know how life began," and, four pages later, "The origin of the solar system is almost as hard to discuss as the origins of life." However, the reader is likely to forget these admonitions after the authors have plunged forthrightly into the unknowable and the undiscussable, supported by an impressive array of figures, tables, equations, diagrams, and structural formulas. The result is a useful review of the present state of scientific speculation and evidence on the subject, the value of which is enhanced by the combination of a succinct presentation with a large amount of specific information, and good, selected bibliographies embellished with helpful annotations. The viewpoint is that of the scientific establishment, and such dissident voices as that of Velikovsky are not seriously considered. A shortcoming is the possibility of inaccuracies that could be seriously misleading, even though they appear to be only typographical. On page 47, for example, the ratio of $[\text{NH}_3]/[\text{NH}_4^+]$ is stated to be 0.06 at pH 80 (*sic!*), surely a degree of alkalinity not even approached on primitive earth, and p_{NH_3} over 1 M NH_3 solution is given as 1.4×10^2 atmospheres, instead of 1.4×10^{-2} .

With this caveat, the book can be recommended both to precocious students and curious established scientists as an introduction to a subject of perennial fascination, and a source of lots of factual data to chew on.

Practical Fluorescence: Theory, Methods and Techniques. By G. G. GUILBAULT (Louisiana State University). Marcel Dekker, New York, N. Y. 1973. xi + 664 pp. \$29.50.

For two decades the monographs "Fluorescence and Phosphorescence" by Pringsheim and "Fluoreszenz Organischer Verbindungen" by Förster have been the books students and scientists have turned to for reviews of fluorescence research. At the time when those books were written (1949 and 1951), it was possible to discuss the topic comprehensively in 300 pages. With the advent of the photomultiplier tube in the early fifties, the field of fluorescence and phosphorescence began to grow rapidly. Now it is a truly formidable task to try to cover all aspects of this highly diversified subject in a single textbook.

The book by Guilbault, which is divided into 16 chapters, emphasizes the practical aspects of luminescence, in particular, analytical

applications. Chapters on instrumentation and measurement techniques describe the practical problems encountered. A chapter contributed by E. L. Wehry discusses the effects of molecular structure and environment on fluorescence. Except for two chapters on the fluorescence of inorganic materials (mainly chelates) and atomic fluorescence flame spectrometry, the book deals with organic substances: assay of organic compounds; fluorescence in enzymology; extrinsic and intrinsic fluorescence of proteins; chlorophyll fluorescence and photosynthesis; fluorescent indicators. In addition, phosphorescence, chemiluminescence, and electrogenerated luminescence of organic compounds are discussed in separate chapters. Two others treat analysis on solid surfaces, and forensic and environmental analysis.

Since the possibilities for artifacts are numerous in fluorescence measurements, the detailed description of experimental difficulties is very useful for the scientist entering this field. An extensive list of references at the end of each chapter, which covers the literature well until 1971, makes it easy to dig more deeply into a particular subject. Although the topics discussed in the various chapters are certainly important, one can think of others of equal interest; for example, I did not find anything on scintillators and optical brighteners. But, in general, the book provides a very good overview of the field of fluorescence and phosphorescence. While the treatment may be too diversified for the student, it will appeal to the scientist seeking acquaintance with this powerful technique.

K. H. Drexhage, *Eastman Kodak Company*

Conduction in Low-Mobility Materials. Edited by N. KLEIN (Technion, Haifa), D. S. TANNHAUSER (Technion, Haifa), and M. POLLAK (University of California, Riverside). Barnes and Noble, New York, N. Y. 1972. xiv + 464 pp. \$32.

This book constitutes the proceedings of the Second International Conference on "Conduction in Low-Mobility Materials" held in Israel in April 1971. The various papers presented were organized around seven themes: Transition Metal Oxides; Low Mobility Transport Theory; Amorphous Semiconductors; Selenium Compounds; Switching Processes; Organic Materials; and Ionic Crystals and Liquids.

The contents consist of review articles and some original contributions, both of theoretical and experimental nature. The emphasis in many of the papers, fortunately, is to discuss experimental findings with a clear aim to examine various aspects of the theory. In general, the papers are of a high standard. The "Discussions" of various papers are not included here, thus diminishing somewhat the value of this otherwise important volume. This book would be of interest to investigators in the field of solid-state science in general and semiconducting materials in particular.

Ashok K. Vijh, *Hydro-Quebec Institute of Research*

A Workbook of Electrochemistry. By J. O'M. BOCKRIS (The Flinders University) and R. A. FREDLEIN (The University of New Castle, Australia). Plenum Press, New York, N. Y. 1973. ix + 177 pp. \$9.95.

Modern electrochemistry, as a broad multidisciplinary science having vital inputs from theoretical electrostatics, solid-state physics, chemical kinetics, heterogeneous catalysis, and interfacial phenomena, has come of age only in the last couple of decades or so. Recently, several books of expository nature that explain the immense impact of "New Electrochemistry" have appeared. None

* Unsigned book reviews are by the Book Review Editor.