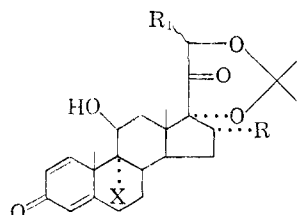


propylidenedioxy-1,4-pregnadiene-3,11,20-trione, m.p. 201–203°, $[\alpha]_D +214^\circ$; 17 α ,21-isopropylidenedioxy-9 α -fluoro-16 α -methyl-1,4-pregnadiene-3,20-dione-11 β -ol (II), m.p. 263–264°, $[\alpha]_D +83^\circ$; 17 α ,21-isopropylidenedioxy-4-pregnene-3,11,20-trione, m.p. 180–185°, $[\alpha]_D +200^\circ$.

The base stability of the isopropylidenedioxy function makes this blocking group useful in corticosteroid synthesis involving vigorous base catalyzed conditions. Compounds containing the isopropylidenedioxy function are particularly useful for the preparation of modified cortical hormones containing an additional substituent at C-21, which is introduced via the enolate ion derived from the free C-20 ketone.

The acetonide function is removed easily from these blocked steroids by heating at steam bath temperatures with aqueous acetic or formic acids for 1 to 2 hours to regenerate the parent steroid in 50–80% yields.



- I, R = H, R₁ = H, X = H
 II, R = CH₃, R₁ = H, X = F
 III, R = H, R₁ = CH₃, X = H
 IV, R = CH₃, R₁ = CH₃, X = F

A side chain modified cortical hormone containing an additional C-21 methyl group was prepared by treatment of (I) with potassium *t*-butoxide in *tert*-butanol with methyl iodide to yield the 21 ξ -methyl derivative (III), m.p. 245°; $[\alpha]_D +93^\circ$; λ_{\max} 244 m μ (13,300). Deacetonation of (III) with 50% acetic acid yielded 21 ξ -methylpredni-

solone which was purified as the 21-acetate, m.p. 218–224°, $[\alpha]_D +97^\circ$; λ_{\max} 244 m μ (14,700).²

In a similar manner the side chain homologation of the biologically potent steroid, dexamethasone,³ proceeding through the intermediates (II) and (IV), m.p. 252–258°; $[\alpha]_D +72^\circ$, yielded 21 ξ -methyl-dexamethasone,⁴ m.p. 243–246°, $[\alpha]_D +79^\circ$, λ_{\max} 239 m μ (15,000).

The biological activity of the 17 α ,21-acetonides of the corticosteroids is of intrinsic interest because of the enhancement of activity in the 16 α -17 α -acetonide of triamcinolone⁵ over the parent steroid. The general utility of the 17 α ,21-isopropylidenedioxy derivatives for the introduction of other substituents at C-21 and for effecting oxidations, halogenations and other base catalyzed transformations with retention of the protective acetonide group will be the subject of a forthcoming publication.

Acknowledgment.—We are indebted to the Schering Corporation for generous financial support of this work.

(2) The physical constants are in agreement with the 21B series reported in a recent publication describing an alternative synthesis of this compound; see E. J. Agnello, R. Plinson, Jr., S. K. Figdor, G. M. K. Hughes, H. W. Ordway, B. M. Bloom and G. D. Laubach, *Experientia*, **16**, 357 (1960).

(3) G. Arth, O. Johnston, J. Fried, W. Spooner, D. Hoff and L. Sarett, *J. Am. Chem. Soc.*, **80**, 3160 (1958); E. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gerbert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Elsler, P. L. Perlman and M. M. Pechet, *ibid.*, **80**, 4431 (1958).

(4) The biological activity of the C-21-methylated compounds in general showed a reduced order (10–30%) of anti-inflammatory activity over the parent unmethylated steroid. We thank Dr. S. Tolksdorf of the Schering Corporation for this information in advance of publication.

(5) J. Fried, A. Borman, W. B. Kessler, P. Grabowich and E. F. Sabo, *J. Am. Chem. Soc.*, **80**, 2338 (1958).

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BOOK REVIEWS

Non-Crystalline Solids. Conference on Non-crystalline Solids, Alfred, New York, September 3–5, 1958. Sponsored by National Academy of Sciences–National Research Council and Air Force Office of Scientific Research, Air Research and Development Command. V. D. FRÉCHETTE Editor, State University of New York College of Ceramics at Alfred University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. xviii + 536 pp. 16 × 23.5 cm. Price, \$15.00.

This book consists of a compilation of twenty papers and discussions representing the proceedings of a conference which brought together leading investigators from several fields for the purpose of clarifying the status of their knowledge and understanding of non-crystalline solids.

The first five chapters deal with scattering of radiation by non-crystalline materials. Electronic structure is treated in chapters 6 to 8. Relaxation phenomena are dealt with in chapters 9 through 12. The final eight chapters are concerned with the structure and properties of special systems. The chapter headings and their authors are:

1. Scattering of Radiation by Non-crystalline Media, P. Debye

2. Spherically Symmetric Fourier Transforms and Medium Range Radial Distribution Functions in the X-Ray Determination of Complex Molecular Structures, D. P. Riley

3. Electron Diffraction Techniques for the Study of Amorphous Systems, S. H. Bauer

4. Structure of Vitreous Silica by Total Neutron Scattering, R. M. Dalaney and A. H. Weber

5. High Temperature X-Ray Diffraction Methods Applied to the Study of Non-crystalline Media. Structure of Molten Fluorides and Chlorides, Jerzy Zarzycki

6. Electronic Band Structure of One-dimensional Disordered Arrays, M. Lax and H. L. Frisch

7. X-Ray Absorption Edge Spectroscopy of Compounds of Chromium, Manganese, and Cobalt in Crystalline and Non-crystalline Systems, Robert A. Van Nordstrand

8. Magnetic Resonance Studies of Glasses, W. P. Slichter

9. The Use and Limitations of Irreversible Thermodynamics in the Study of Relaxation Processes, R. O. Davies

10. Liquid Relaxation Phenomena and the Glass State, Theodore A. Litovitz

11. Kinetics of Mechanical Relaxation Processes in Inorganic Glasses, P. L. Kirby
12. Non-Newtonian Relaxation in Amorphous Solids, Sang Joon Hahn, Taikyue Ree, and Henry Eyring
13. Amorphous Sulfur and Selenium, J. A. Prins
14. Kinetics of Ion Motion in Anodic Oxide Films, D. A. Vermilyea
15. Amorphous Layers and Their Physical Properties, R. Hilsch
16. The Chemical Approach to Problems of the Glassy State, R. W. Douglas
17. Network Defects in Non-crystalline Solids, J. M. Stevels
18. The Anomalous Properties of Vitreous Silica, O. L. Anderson and G. J. Dienes
19. Strength of Amorphous Solids, R. J. Charles and J. C. Fisher
20. The Thermal Conductivity of Glass, P. G. Klemens

The discussions following each chapter are a very important aspect of the book. Here, additional results and interpretations are given often in a thought-provocative manner, highlighting the many questions that still remain. In at least one instance, the discussions brought out an important omission in the main presentations by pointing out the application of nuclear electric quadrupole resonance spectroscopy to the non-crystalline state, a technique which has promising potentiality in this research area.

At the end of each chapter the pertinent references are included, supplying the specialist with references from other fields which may ordinarily escape him.

Some of the chapters treat the experimental and theoretical aspects of certain techniques and then follow with applications to the non-crystalline state. Some of these methods have been discussed in a number of recent books and consequently represent a repetition of material that is covered as well or better in other easily available sources. A reader who is familiar with such coverage may feel a pertinent reference would eliminate the necessity of duplication and then the writer could devote the corresponding space to a crucial discussion of more of the applications to the problem of interest, *i.e.*, non-crystalline solids. However, it is a convenience to the reader to have the technique summarized between the covers of one book and it undoubtedly contributes to the smoothness of the presentation.

The book is well edited and the articles are written in a clear and readable fashion. The book will be a useful addition to the libraries of individuals interested in non-crystalline solids and it will encourage research workers to apply techniques from fields of science other than their own to this important research area.

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Proceedings of the Symposium on the Mechanism of Heterogeneous Catalysis. 12-13 November, 1959, Amsterdam, The Netherlands. Edited by J. H. DE BOER. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey, 1960. ix + 180 pp. 13 × 19 cm. Price, \$3.00.

This symposium volume stands out as exceptional in the morass of symposia which are being announced in the lists of technical publishers with increasing frequency. With the shortening of transportation time between the various scientific centers of the world, symposia, with hundreds of participants from many lands, each bringing digests of earlier publications, are proliferating in abundance. Participants concede, when the proceedings are concluded, that the antechambers of the symposium were more fruitful in scientific exchange than the lecture halls. But that condition does not help the purchaser of the subsequent volume.

This monograph on heterogeneous catalysis is distinguished by the fact that there are nine contributions in 177 pages and one of these only two pages long, in summary, because the material had already been published elsewhere. There were 27 participants in the discussions and their very significant participation is recorded in the total number of pages already mentioned. All the authors and participants lived in Holland so transportation expenses were minimal. The end-product abundantly justifies the

hope expressed by the Chairman, Professor Dr. J. H. de Boer, that it will be "well received not only in the Netherlands, but in other countries as well." Authors' and discussants' views have therefore been given in English, although the symposium language was Dutch.

Anyone who wishes to learn the main features, as of November, 1959, of current aspects of heterogeneous catalysis, as to general theory of mechanism, electronic and chemical factors in heterogeneous catalytic change in gas phase or solutions, with decomposition of formic acid or the synthesis of ammonia as typically standard examples, of Ziegler catalysts, selective hydrogenation, and, finally, bifunctional catalysis, cannot do better than purchase this volume. In two sessions of evening reading he can, thanks to our Dutch brethren, be brought abreast of current thought in catalysis, probably more effectively than by prolonged reading of volumes five-fold in size that are appearing at frequent intervals. The book is as excellent and pleasurable as a well-engineered small car.

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Archives de l'Institut International des Sciences Théoriques. Fascicule 10. Théorie Fondamentale du Système Périodique des Eléments. By S. DOCKX, O. P., Directeur de l'Institut. Office International de Librairie, 30 Avenue Marnix, Bruxelles 5, Belgium. 1959. 183 pp. 16.5 × 24.5 cm. Price, BF 300,—.

Chemical similarities and the masses of the atoms formed the back-ground for the early representation of the periodic system of the elements. Much later it became possible to explain the periodicity, in terms of electronic configurations, arrived at by extrapolating the properties of the hydrogen atom to the other atoms and combining this with the Pauli principle. In quite a few cases, however,—transition elements, rare earths and actinides—the assignment of a certain electronic configuration to a certain atom has not been unambiguous.

In this book an attempt is made to get rid of these ambiguities. The author sets up a series of theorems (which are actually postulates), concerning the filling of the sub-shells. By means of these postulates he is able to construct a periodic system in which the rare earths and the actinides are included in a "natural" way instead of being placed in separate "boxes" below the main table. In the cases where his electronic configurations differ from the ordinarily accepted ones, the author supports his results with recent experimental evidence. The periodic system presented in this way is certainly esthetically more appealing than the ordinary one. Which one is the more "correct," is, however, very difficult to say. The whole question is tied up with the problem as to whether it is meaningful at all to use the shell-approximation for large atoms.

The second part of the book is unfortunately invalidated by conclusions, which are contradictory to the basic theory of angular momenta for atoms. The author seems to be unaware of the fact that the quantum numbers J , L , S (or rather $J(J+1)$, $L(L+1)$, $S(S+1)$), are the eigenvalues of the operators J^2 , L^2 , S^2 , and as such never negative. From the author's notation one gets the impression that he has mixed up the two types of quantum numbers J , L , S and M_J , M_S .

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3^e Colloque de Métallurgie sur la Corrosion (Sèche et Aqueuse). Organisé à Saclay les 29-30 juin et 1^{er} juillet, 1959. Organized by M. SALESSE, Chef du Département de Métallurgie. North-Holland Publishing Company, P. O. Box 103, Amsterdam, Holland. 1960. 241 pp. 21 × 28 cm. Price, \$10.00.

This is yet another of the many "books" based on collecting papers given at a meeting, symposium or conference. There is some discussion to act as cementing material, but by and large this volume, like others similar to it, does not deserve review as a book. To do so would be much the same