Germanium tetrachloride vapor was passed at the rate of 30 mmoles/hr. through 10 mm. o.d. Pyrex tubing which passed through a microwave resonance cavity similar to that described by Zelikoff, *et al.*[3] The pressure of germanium tetrachloride vapor at the entrance to the cavity was approximately 0.1 mm. At the immediate exit of the discharge cavity, a yellow solid and a viscous pale yellow oil collected in an amount roughly equal to that of the Ge_2Cl_6 collected. These relatively non-volatile products have not been further characterized. The effluent vapors passed, successively, through a −18° trap (which condensed the Ge_2Cl_6), a −78° trap (which condensed the undecomposed $GeCl_4$), and a −196° trap (which condensed the chlorine).

Digermanium hexachloride is a colorless, crystalline material which is sublimed easily at room temperature; the observed melting range is 40–42°. A sample has been analyzed for germanium after hydrolysis and oxidation with hydrogen peroxide by titration of the germanic acid in the presence of mannitol. Chlorine analyses have been performed after hydrolysis both by the Mohr method and by titration of the liberated hydrochloric acid. The average oxidation state of the germanium has been measured by titrating a 3 *M* HCl solution of a sample with iodine. *Anal.* Calcd. for Ge_2Cl_6: Ge, 40.57; Cl, 59.43; ox. state of Ge, +3. Found: Ge, 44.9; Cl, 59.2 (Mohr) and 57.9 (from HCl); ox. state of Ge, +3.04.

We wish to thank Mr. Jack Frazer for the use of the Baird Associates' Hg 198 Exciter. This work was performed under the auspices of the U. S. Atomic Energy Commission.

[3] M. Zelikoff, P. H. Wyckoff, L. M. Aschenbrand and R. S. Loomis, *J. Opt. Soc. Am.*, **42**, 818 (1952).

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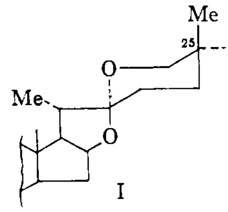
RECEIVED NOVEMBER 1, 1958

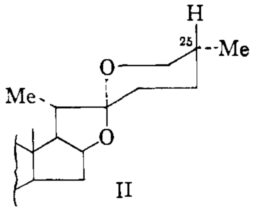
THE MECHANISM OF THE ISOMERIZATION OF STEROIDAL SAPOGENINS AT C-25

Sir:

Extensive previous investigations have established that the normal (I) and the iso (II) sapogenins differ in configuration only at C-25.[1] In the light of this fact, the acid-catalyzed interconversion[2] of the isomers appears remarkable. Cornforth has suggested[1,3] that the reaction might involve bimolecular displacement by a proton, with inversion, but such a reaction is without parallel in organic chemistry.

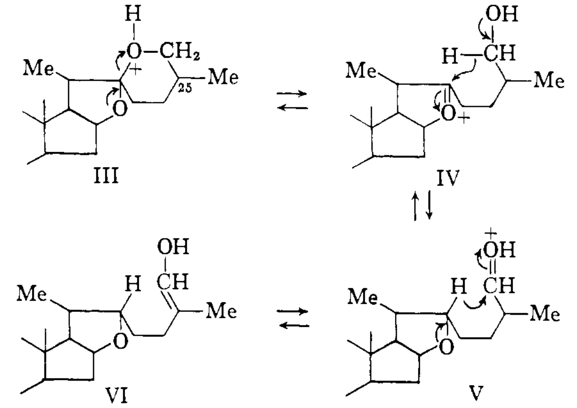


I

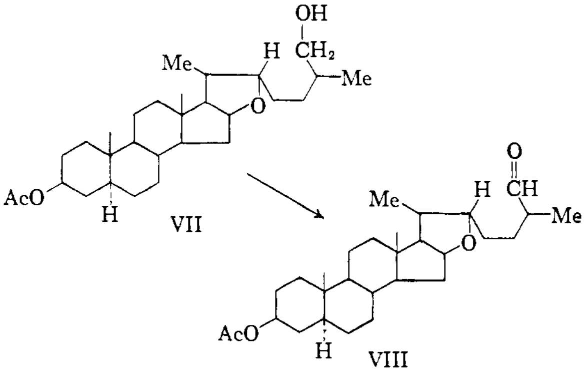


II

We consider that the isomerization proceeds by an oxidation–reduction mechanism. The key step in the change is a reversible hydride transfer involving the oxonium compounds (IV) (available by the simple change III ⇄ IV) and (V).[4] Since the conjugate acid V may be expected to be in readily established equilibrium with the corresponding enol VI, change in configuration at C-25 is simply accommodated.



We have found powerful support for our mechanism in the observation that the change V → IV does in fact occur readily. Dihydrotigogenin 3-monoacetate (VII)[5] in benzene was oxidized by sodium dichromate in aqueous sulfuric acid/acetic acid. Chromatography of the reaction mixture on alumina gave an oily mixture of the aldehydes VIII, isomeric at C-25, from which one pure component [m.p. 86–87°, $[\alpha]_D$ −16° ($CHCl_3$), λ_{max} 3.62 μ; Found: C, 75.81; H, 10.30] separated. Re-chromatography of the crystalline isomer regenerated the stereoisomeric mixture. When the crystalline aldehyde, or the mixture, was subjected under nitrogen to the conditions ordinarily used[2] to bring about the interconversion of I and II (concentrated hydrochloric acid in boiling ethanol), tigogenin admixed with some neotigogenin was produced in over 75% yield in two hours. From this mixture, pure tigogenin [m.p. 202–204°, $[\alpha]_D$ −49° (C_5H_5N)], identical with authentic



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[1] R. K. Callow and P. N. Massy-Beresford, *J. Chem. Soc.*, 2645 (1958), and earlier references there cited.

[2] R. E. Marker and E. Rohrmann, THIS JOURNAL, **61**, 846 (1939); R. K. Callow and V. H. T. James, *J. Chem. Soc.*, 1671 (1955); M. E. Wall, S. Serota and L. P. Witnauer, THIS JOURNAL, **77**, 3086 (1955).

[3] J. W. Cornforth, *Ann. Repts. on Progr. Chem. (Chem. Soc. London)*, **50**, 219 (1953).

[4] It may be noted that hydride-transfer reactions of a related type are known (*cf.* P. D. Bartlett and J. D. McCollum, THIS JOURNAL, **78**, 1441 (1956)).

[5] Y. Sato and H. G. Latham, *ibid.*, **78**, 3150 (1956).

material, was isolated in *ca.* 70% yield. Further, the aldehyde VIII was converted smoothly to tigogenin acetate [m.p. 200–202°, $[\alpha]_D$ $-74°$ $(CHCl_3)$] when it was treated with boron trifluoride etherate in benzene for sixteen hours at room temperature. In blank experiments, *no* tigogenin was produced from dihydrotigogenin monoacetate (VII) by treatment with acidic reagents.

It may be noted that the recent deuterium exchange experiments of Callow and Massy-Beresford[1] are entirely in accord with the isomerization mechanism here proposed.

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BOOK REVIEWS

The Effects of Ionizing Radiation on Natural and Synthetic High Polymers. By FRANK A. BOVEY, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1958. xiii + 287 pp. 16 × 23.5 cm. Price, $8.00.

Under the editorship of Professor H. Mark a new series of books on polymers has been started, a series entitled "Polymer Reviews" of which the first is this interesting book written by F. A. Bovey, on radiation effects in polymers. Professor Mark is to be congratulated for initiating this series; we look forward to additional volumes as time goes on.

The first two chapters of Dr. Bovey's book summarize the properties of ionizing radiations and the chemical effects produced by them in gases and condensed systems. The subject matter of these two chapters is well organized and clearly written, but it constitutes in no sense a complete or authoritative discussion of the subject. For example, while radiation sources are briefly described and illustrated by photographs, the reader will find here no helpful details, such as thickness of shielding required or detailed designs of radiation cells. The author is uncertain whether to recommend 20 or 15.5 for $G(Fe^{+++})$ in the Fricke dosimeter. However, these first two chapters do constitute a good introduction to the subject of radiation chemistry.

Next comes a chapter summarizing the history of ionizing effects in high polymers, crosslinking and scission, effect of oxygen, protection and promotion, and the general effects of ionizing radiations on the physical, chemical and electrical properties of high polymers. In the historical section references to the early American[1] and Soviet[2] work are missing. The discussion of crosslinking and scission emphasizes such effects, probably because of their importance in influencing properties of industrial interest, while at the same time the production and decay of unsaturation are hardly mentioned. The section on the general effects of oxidation is as good as could have been written considering the incomplete knowledge of the mechanism and kinetics of radiolytic oxidation existing at the time the book was written (and even today, for that matter). In discussing protective action and energy transfer effects, the author correctly describes the important work of Manion and Burton, but Fig. III-I(b) illustrates the independence of effects and no energy transfer in mixed benzene and toluene, rather than any protective action. The fourth chapter describes and simplifies in a well written manner, mathematical theories of gelation, crosslinking, scission, branching and endlinking and various combinations of these effects. This is probably the best chapter of the book and exemplifies the author's own interest in these aspects of the radiation chemistry of polymers.

The rest of the book contains chapters in which specific solid polymers are considered one after the other. With a few exceptions, everything that has been discovered through the year 1956 about the action of ionizing radiations on solid polymers is mentioned. Subjects completely omitted are (1) the use of ionizing radiations in promoting the polymerization of monomers, and (2) the production of graft polymers. Perhaps these subjects are reserved for later volumes in the series. The last chapter on natural macromolecules, such as cellulose, proteins, viruses, etc., contains an interesting account of radiation effects in this complex field. Again, it is only an introduction, but a good one, and not an authoritative treatment. For example, the author interprets the results of Fricke on egg albumin as due to "hidden" breaks in the polypeptide chain, for which there is no conclusive evidence.

Surprisingly, the subject of the oxidation of polymers during irradiation has been poorly handled. Thus, the important paper of Sears and Parkinson[3] in which post-irradiation oxidation effects were first described is not mentioned. If the author had read the first American work[1] on polyethylene, he would not have concluded that the results of Lawton, Balwit and Powell demonstrate that "carbonyl formation in polyethylene is mainly a postirradiation effect." The significant observations of Chapiro[4] are quite inadequately described. Admittedly we have much learned, but even in 1956 we knew more than the reader of Dr. Bovey's book would infer.

In his foreword Professor Mark expressed the hope that this volume will be stained by chemicals while left lying on working benches in laboratories rather than remaining clean and neat standing on library shelves. Because of his excellent organization and comprehensive coverage of this extremely active branch of polymer chemistry, it is quite evident that Dr. Bovey's book will fulfill Professor Mark's expectations. Those of us who are working in this field will be indebted to Dr. Bovey for many years for his helpful review.

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(1) M. Dole, Report of Symposium IV. "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Md., 1950, p. 120.

(2) V. L. Karpov, "Conference of the Academy of Sciences of the U.S.S.R. on the Peaceful Uses of Atomic Energy," July 1, 1955, English Translation U.S. Atomic Energy Commission, Washington, D.C., 1956.

(3) W. C. Sears and W. W. Parkinson, Jr., *J. Polymer Sci.*, **21**, 325 (1956).

(4) A. Chapiro, *J. chim. phys.*, **52**, 246 (1955).

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The Properties of Gases and Liquids. Their Estimation and Correlation. By ROBERT C. REID, Associate Professor of Chemical Engineering, Massachusetts Institute of Technology, and THOMAS K. SHERWOOD, Professor of Chemical Engineering, Massachusetts Institute of Technology. McGraw-Hill Book Co., Inc., 330 West 42nd Street, New York 36, N. Y. 1958. xii + 386 pp. 16 × 23.5 cm. Price, $10.00.

One of the most important problems facing design engineers is the accurate prediction and extrapolation of physical data. This book is a summary of methods available