me by Dr. Oliver H. Emerson. Its insolubility in alkalies and its high reducing power, as well as the lack of reducing properties in its esters are also in good agreement with such an assumption.

My present efforts are mainly directed to an elucidation of the alkyl portion of α-tocopherol. On completion of these investigations I intend to publish the details of the above experiments. I wish to express my appreciation of the assistance of Professor H. M. Evans and Dr. Oliver H. Emerson of the University of California who kindly advised me on the production of α-tocopherol and who assayed various concentrates during its preparation.

RESEARCH LABORATORIES E. FERNHOLZ
MERCK & COMPANY, INC.
RAHWAY, N. J.

RECEIVED MAY 20, 1937

CIS-TRANS ISOMERIZATION BY BROMINE ATOMS

Sir:

An investigation to ascertain whether halogens and halogen acids add "*cis*" or "*trans*" to maleinoid (*cis*) or fumaroid (*trans*) forms of unsaturated substances has been under way in this Laboratory for some time. It is evident that for a complete understanding of this problem it is necessary to know the effectiveness of the addition reagent causing the transformation of the "maleinoid" and the "fumaroid" form. Yet, while numerous observations on the rearrangement in solution of the "maleinoid" to the "fumaroid" form are available, no critical study has been made of the inter-relationship of the reagents responsible for the transformation, and no comprehensive hypothesis has been advanced which would correlate these diverse observations.

We have found that in the dark, in two hours, carefully purified isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide when the reactants are mixed either in air or in a highly evacuated tube, or in the presence of antioxidants (*e. g.*, hydroquinone, catechol, thiophenol). However, the addition of a peroxidic substance (*e. g.*, benzoyl peroxide, ascaridole) to the reaction mixture caused complete isomerization to stilbene in a few minutes. The time required for complete conversion varied with the amount of the peroxide used, but even minute traces of peroxides caused complete conversion in thirty minutes.

In direct sunlight or in artificial light, isostilbene, dissolved in benzene, is transformed to stilbene by hydrogen bromide in about five minutes. Here evacuation of the reaction vessel had a pronounced effect in that twenty minutes was required for complete isomerization. Most striking, however, is the effect of antioxidants. Thus, hydroquinone, ethyl mercaptan, etc., completely prevent the transformation of isostilbene to stilbene by hydrogen bromide in the light, either in the presence or absence of air.

Furthermore, no isomerization of isostilbene to stilbene was observed under any of the above conditions (antioxidant or peroxidic, in the light or in the dark) with hydrogen chloride. Neither has a mixture of bromine and hydrogen bromide caused isomerization in the dark. The halogens are well known to cause isomerization in the light.

The above experiments lead us to believe that bromine atoms[1] are the active catalysts in this transformation. They would be produced by the action of oxygen or a peroxide, or by light, on hydrogen bromide. Once produced, they convert isostilbene to stilbene by a chain reaction. The ineffectiveness of hydrogen chloride in causing isomerization is thus readily explainable on the basis of its relative stability toward oxygen.

Several investigators[2] have observed that alkali metals and traces of certain organo-alkali compounds cause similar isomerizations. We are, therefore, engaged in an extensive study to evaluate the part played by atoms in such conversions, and the role of other agencies.

(1) The hypothesis that bromine atoms are responsible for the "peroxide effect" in the addition of hydrogen bromide to unsaturated molecules is proposed in an article by M. S. Kharasch, H. Englemann and F. R. Mayo, in the *Journal of Organic Chemistry*, in press.

(2) Meerwein and Weber, *Ber.*, **58**, 1266 (1925); Schlenk and Bergmann, *Ann.*, **463**, 107–117 (1928); Ziegler and Wollschitt, *ibid.*, **479**, 129–131 (1930).

JONES CHEMICAL LABORATORY M. S. KHARASCH
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RECEIVED MAY 18, 1937

PHOTODECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE SOLUTION

Sir:

We have investigated recently the bromine sensitized photodecomposition of chlorine dioxide in carbon tetrachloride solution and find that appreciable amounts of Cl_2O_6 are formed during the reaction. A reinvestigation of the unsensitized decomposition of chlorine dioxide in carbon tetrachloride solution using $\lambda = 3650$ Å, showed that here also relatively large amounts of Cl_2O_6 are formed.

Chlorine dioxide solutions were insolated for some time and then forced into water and shaken. A heavy mist was observed similar to that which forms when Cl_2O_6 reacts with water. Chlorine dioxide and chlorine were removed from the water extract by aspirating air through it for three hours. The resulting solution was neutralized with potassium hydroxide and evaporated. Microscopic examination of the crystals obtained indicated potassium chlorate and potassium perchlorate. The presence of ClO_4^- was also demonstrated by characteristic crystals formed when a drop of 2% brucine solution was added to a drop of the test solution on a microscope slide. The outside of the spot was surrounded by a brown ring which is also characteristic of ClO_3^-. The tests were compared with similar tests on pure substances. The chloric acid and perchloric acid can be explained by the formation of Cl_2O_6 which reacts with water according to

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

Qualitative tests on the water extract also indicated small amounts of hypochlorous acid, presumably due to Cl_2O.

$$Cl_2O + H_2O \longrightarrow 2HClO$$

Methods for the quantitative estimation of chlorine dioxide, chlorine, hypochlorous acid, chloric acid and perchloric acid in the water extract have been developed and checked. The relative amounts of the different components depend in a rather complicated way upon such factors as concentrations, light intensity and time of insolation. This is to be expected since Cl_2O_6 and Cl_2O are themselves photosensitive.

The point which we wish to stress in this note is that relatively large amounts of Cl_2O_6 are formed (corresponding in some experiments to as much as 20% of the chlorine dioxide decomposed). This is in contradiction to the findings of previous workers [E. J. Bowen, *Trans. Faraday Soc.*, **27**, 513, (1931); Y. Nagai and C. F. Goodeve, *ibid.*, **27**, 508, (1931)], who report only chlorine and oxygen. The formation of Cl_2O_6 indicates that the above reactions in solution probably have mechanisms similar in many respects to those for the corresponding gaseous reactions [THIS JOURNAL, **56**, 269 (1934)].

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SASKATCHEWAN
SASKATOON, SASK., CANADA
J. W. T. SPINKS
H. TAUBE

RECEIVED APRIL 22, 1937

NEW BOOKS

The Chemistry of Natural Products Related to Phenanthrene. By L. F. FIESER, Associate Professor of Chemistry, Harvard University. Second edition, with an appendix. Reinhold Publishing Corporation, 330 West 42d Street, New York, N. Y., 1937. xiv + 456 pp. 15.5 × 23.5 cm. Price, $7.00.

The increased activity and interest in the field of phenanthrene and related compounds have led the authors of this useful and widely accepted book to supplement the second edition with an appendix. This consists of about 90 pages devoted to a description and discussion of the published investigations during 1936.

The topics are grouped in individual chapters which correspond to those in the main portion of the book. They are too numerous to review here but they include the important contributions to the structure of Vitamin D and the stereochemical nomenclature of the sterols, androsterone and analogous compounds. This additional part has been written with the same clarity and completeness as characterized the original work.

The second edition of this book will be of inestimable value to the investigator or scholar in this general field, as it offers a comprehensive résumé of the literature up to January 1, 1937.

ROGER ADAMS

Reagent Chemicals and Standards, with Methods of Assaying and Testing them; also the Preparation and Standardization of Volumetric Solutions and Extensive Tables of Equivalents. By JOSEPH ROSIN, Chief Chemist and Chemical Director, Merck & Company, Inc. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1937. x + 530 pp. 16 × 23.5 cm. Price, $6.00.

This volume is a thoroughly modern and carefully edited treatment of approved methods for testing the commoner chemical reagents, and the standards of purity to be sought. The author, working from the Merck-Krauch book originally published in 1888, the Murray