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 λ = 3650 Å, showed that