The Isomerization of Isostilbene to Stilbene by Hydrogen Bromide in the Presence of Oxygen and of Ferromagnetic Metals.

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In the previous paper⁽¹⁾ the authors reported that hydrogen bromide, in presence of oxygen, accelerated the isomerization of isostilbene to stilbene in the dark at room temperature in absence of solvents, while neither hydrogen bromide nor oxygen was active when present alone. However, M. S. Kharasch, J. V. Mansfield, and F. R. Mayo⁽²⁾ observed that isostilbene in benzene solution was not isomerized to stilbene by hydrogen bromide even when the reactants were mixed in air (but the addition of a peroxide to the reaction mixture caused a rapid isomerization). With a view to obtaining an explanation of this apparent contradiction the present authors have studied the isomerization by hydrogen bromide in presence of oxygen in benzene solution.

Reduced nickel was found also to co-operate with hydrogen bromide to accelerate the isomerization of isostilbene to stilbene, although the effect of hydrogen bromide in presence of reduced nickel was much smaller than in presence of oxygen.⁽¹⁾ Another ferromagnetic metal, reduced iron, as well as other metals have now been examined in the isomerization by hydrogen bromide in absence of solvents, and reduced nickel in the isomerization in benzene solution. Further, the influences of antioxidants on the isomerization by hydrogen bromide in presence of oxygen or reduced nickel have been investigated.

Isostilbene was prepared, according to the directions of Schlenk and Bergmann,⁽³⁾ by hydrogenating tolane in presence of palladium on barium sulphate, b.p. 110–110.5° under 1.2 mm., n_D^{20} 1.6130. Hydrogen bromide was prepared by the action of purified bromine on hot tetralin, washed by passing through cold tetralin and over moist red phophorus, then dried with anhydrous calcium bromide and with phosphorus pentoxide. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen, and reduced copper by grinding copper oxide in wire form (Merck) and reducing with hydrogen. Other materials were the purest commercial products, which were used directly or after purification.

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(1) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.
(2) *J. Am. Chem. Soc.*, **59** (1937), 1155.
(3) *Ann.*, **463** (1928), 115.

I. Isomerization in Presence of Oxygen in Benzene Solution. The experiments in benzene solution resulted similarly to those without the solvent: A benzene solution containing 5 per cent isostilbene was saturated with air and was made 0.01 N in hydrogen bromide by adding an appropriate amount of a concentrated benzene solution of hydrogen bromide in the dark at room temperature. After 20–30 minutes, the solution was washed with water, dried over anhydrous sodium sulphate, and evaporated. The residue, from which stilbene already began to crystallize out at the temperature of the boiling water bath (stilbene more than 50%), solidified to a crystalline mass on cooling. Thus it may be suspected that in the American investigators' experiments no sufficient oxygen was absorbed when the reactants were mixed in air or the result of the reaction was examined too soon.

When a much larger amount of hydrogen bromide was used (in presence of oxygen in benzene solution in the dark at room temperature), the first change was of course the isomerization of isostilbene to stilbene, but after 20 hours from beginning it was noticed that stilbene dibromide (m.p. 237°, identified with an authentic specimen) had been formed. This observation may favour the theory of bromine atoms by Kharasch and co-workers,⁽²⁾ although they did not notice the effect of oxygen (air) on the isomerization of isostilbene to stilbene by hydrogen bromide in benzene solution.

II. Isomerizations in Presence of Reduced Iron and of Other Metals without Solvents, and in Presence of Reduced Nickel in Benzene Solution. In the same manner as in the previous experiments with reduced nickel,⁽⁴⁾ the four metal catalysts, reduced iron, platinum black, palladium black, and reduced copper, were examined in their effects on the isomerization of isostilbene by hydrogen bromide. Reduced iron showed an effect comparable to that of reduced nickel, the crystals of stilbene beginning to appear in the course of ½–4 hours according to the amount of hydrogen bromide. The other metals gave also positive results, but it was more than 20 hours before crystals began to separate out. Although no exact comparison of the effects of these metals is possible, it may be mentioned that the ferromagnetic reduced nickel and reduced iron produce a stronger accelerating effect on the isomerization in co-operation with hydrogen bromide than the other metal catalysts so far used.

In the benzene solution (4 c.c.), containing 5–10 per cent isostilbene and 0.015–0.08 N hydrogen bromide, the formation of stilbene could not

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(4) This Bulletin, **12** (1937), 508.

be demonstrated in presence of reduced nickel (0.1–0.5 g.) in the course of 1–4 days (in the dark at room temperature), a slightly viscous yellowish liquid being recovered. Such was also the case in absence of reduced nickel. However, in presence of reduced nickel and a large amount of hydrogen bromide a small quantity of stilbene was formed. Stilbene dibromide was not found in this case (examined on the fourth day). Thus it seems that the activity of reduced nickel is diminished to a great extent for the given concentrations of the reactants in benzene solution.

III. **Influences of Antioxidants.** When isostilbene, sealed with hydrogen bromide in a glass tube in absence of air, was exposed to sunlight, stilbene began to separate out in crystals in ½–1 minute and then the whole solidified instantly to a crystalline mass. The addition of catechol to isostilbene prevented the isomerization by hydrogen bromide in sunlight. Diphenylamine, which can eliminate more or less the effect of oxygen and peroxides in the addition of hydrogen bromide to unsaturated compounds, was found not to share with catechol the property of preventing the isomerization of isostilbene by hydrogen bromide in the light: When isostilbene containing diphenylamine was exposed to sunlight in presence of hydrogen bromide, stilbene separated out within a minute. It may be added here that in the dark isostilbene was not isomerized by diphenylamine either in presence or in absence of hydrogen bromide.(5)

Catechol prevented also the isomerization by hydrogen bromide in the heat: When isostilbene (0.2 c.c.) and hydrogen bromide (3 c.c.), sealed in a glass tube in absence of air, were heated in boiling water in the dark, the isomerization became noticeable in 30 minutes (stilbene crystallized out on cooling), while the addition of catechol (5 mg.) prevented this isomerization.

The influences of catechol and of diphenylamine on the isomerization of isostilbene by hydrogen bromide in presence of reduced nickel and of oxygen were also investigated.

Reduced nickel (20 mg.) was taken in a reaction tube, and isostilbene (0.2 c.c.) with catechol (5 mg.) in a side tube attached to the reaction tube. The nickel was heated at 330–350° in the atmosphere of hydrogen and then in vacuum, and cooled in vacuum. Hydrogen bromide (5 c.c.)

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(5) According to G. R. Clemo and S. B. Graham, *J. Chem. Soc.*, **1930**, 213, dimethyl maleate is isomerized to dimethyl fumarate by primary and secondary amines. However, neither dimethyl maleate nor isostilbene was found to be transformed into the corresponding trans compound by diphenylamine.

was introduced, and the tube sealed off. The isostilbene containing catechol was decanted on the reduced nickel. After the mixture was left to stand in the dark at room temperature for a certain time, the tube was cut open in an aqueous solution of caustic soda, thus the access of air while hydrogen bromide was still present being avoided. In this experiment it was found that catechol prevented the isomerization of isostilbene by hydrogen bromide in presence of reduced nickel over 40 hours. On the other hand, diphenylamine could not prevent the isomerization under the same conditions as above. When isostilbene containing diphenylamine was first decanted on the reduced nickel and then hydrogen bromide was introduced, the result was the same (isomerization proceeded indifferently to diphenylamine).

Catechol prevented also the isomerization of isostilbene by hydrogen bromide in presence of oxygen, stilbene being not formed in the course of 20 hours. The inhibiting influence of diphenylamine on the isomerization by hydrogen bromide in presence of oxygen was also noticeable but weaker than that of catechol, about 20 per cent of isostilbene being transformed into stilbene in an hour.

Thus, the influences of the antioxidants on the isomerization of isostilbene by hydrogen bromide in presence of oxygen and of reduced nickel showed a certain parallelism to the influences of antioxidants on the effects of oxygen and of reduced nickel in the addition of hydrogen bromide to allyl bromide(6) and to undecenoic acid.(7) In every case, catechol eliminates to a great extent the effects of oxygen and of reduced nickel; on the other hand, diphenylamine, while it prevents more or less the action of oxygen, is incapable of influencing the effect of reduced nickel.

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(6) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 400.

(7) Y. Urushibara and M. Takebayashi, *ibid.*, **13** (1938), 404.