The Isomerization of Methyl Allo-cinnamate by Hydrogen Bromide and the Influence of Oxygen.

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In the previous report⁽¹⁾ an observation concerning the isomerization of dimethyl maleate to the fumarate caused by hydrogen bromide and chloride was described. It was shown that no participation of oxygen in addition to hydrogen bromide is necessary and this type of conversion of cis-trans isomerides was contrasted with that of isostilbene to stilbene⁽²⁾, which is brought about by the joint action of hydrogen bromide and either oxygen or reduced nickel but not by hydrogen bromide alone nor by hydrogen chloride under any condition at room temperature. In view of the essential function of the carbomethoxyl group in correlation to which were interpreted the experimental results and of hitherto attempted explanations of the nature of the catalysis by hydrogen halides in the

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(1) O. Simamura, this Bulletin, **14** (1939), 22.

(2) Y. Urushibara and O. Simamura, *ibid.*, **12** (1937), 507; **13** (1938), 566.

isomerization, a mechanism was tentatively suggested that the hydrogen halide associates with the ethenoid compound by the formation of hydrogen bond through the carbonyl oxygen atom, the accompanying displacement of the shared electrons in the molecule resulting in the more or less diminished rigidity of the double bond.

The scope of the research has since been extended to methyl allo-cinnamate, which has been, in conformity with the expectation from its structure, found to display the behaviour intermediate between dimethyl maleate and isostilbene. Thus, hydrogen bromide converted methyl allo-cinnamate to methyl cinnamate in the dark at room temperature with a slower rate than dimethyl maleate, and the isomerization was accelerated by the presence of oxygen, the action of which was suppressed by catechol added beforehand to the ester. Methyl allo-cinnamate was isomerized by hydrogen chloride very slowly even at an elevated temperature (55°). The formation of methyl cinnamate was also brought about by the addition of a drop of piperidine⁽³⁾ to 0.1 c.c. of the allo-cinnamate (34% in the course of 24 hours).

These facts add to the possibility of the proposed mechanism of the catalysis by hydrogen halides, in which the presence of a carboalkoxyl group or rather of a carbonyl group conjugated with the double bond is essential. Further, in support of this view it is recorded in the literature that dibenzoyl-ethylene⁽⁴⁾ and isobenzaldesoxybenzoin⁽⁵⁾ are easily converted by hydrogen chloride into their geometrical isomerides. According to the recent study by Y. Urushibara⁽⁶⁾ bromine atoms play a deciding part as chain carriers in the addition of hydrogen bromide to allyl bromide in the presence of oxygen and in the isomerization of isostilbene by the co-operative action of hydrogen bromide and oxygen. As photo-sensitized bromine catalysis in the cis-trans isomerization is widely observed, it seems that the co-operation of hydrogen bromide and oxygen may be rather general irrespective of the nature of the substituents in the isomerizing molecule. In the case of dimethyl maleate the failure of detection of the influence of oxygen may be ascrided to the rapidity of the hydrogen bromide catalysis. With methyl allo-cinnamate the effectiveness of oxygen has been demonstrated.

Materials. The hydrogenation of methyl phenylpropiolate to methyl allo-cinnamate in methanol with palladium deposited on barium sulphate as catalyst yielded a mixture, which could not be easily handled. Then sodium phenylpropiolate was hydrogenated in aqueous solution with the same catalyst to allo-cinnamic acid (Yield 20%), which was converted into the silver salt and finally into the methyl ester by the action of methyl iodide upon the latter suspended in dry ether in the dark at room temperature.⁽⁷⁾ The raw product was once distilled in vacuum, b.p. 94° under 1–1.5 mm., n_D^{20} 1.5541. Other materials were obtained and purified as described in the previous report.⁽¹⁾

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(3) Compare G. R. Clemo and S. B. Graham, *J. Chem. Soc.*, **1930**, 213.
(4) C. Paal and H. Schulze, *Ber.*, **35** (1902), 168.
(5) H. Stobbe and K. Niedenzu, *ibid.*, **34** (1901), 3897.
(6) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.
(7) C. Liebermann, *Ber.*, **23** (1890), 2510; **24** (1891), 1107.

Experimental. A clearing point curve of the binary mixture methyl allo-cinnamate—methyl cinnamate was constructed from the following data and subsequent analyses of reaction mixtures were effected by reference to the curve.

Cinnamate (%)	0	10.9	17.7	30.9	39.7	55.4	72.6	85.0	100
Clearing point (°C.)	−3	−7	−9	−4	4.5	17	25.5	31.5	35

Experiments were carried out in the dark at room temperature, procedures being much the same as with dimethyl maleate. In a small glass bulb 0.1 c.c. of methyl allo-cinnamate was taken and after evacuation of the bulb 10 c.c. of hydrogen bromide was introduced, the bulb sealed off and left to stand for about two hours. Then the sealed end of the bulb was crushed in 1% aqueous potassium hydroxide, the oil was taken up in ether, the ether solution washed with water, dried and evaporated. The resulting ester mixture contained 71% of methyl cinnamate. When in addition to hydrogen bromide 3 c.c. of oxygen was admitted, as much as 82% of the allo-cinnamate was isomerized; and 15 mg. of catechol inhibited completely this accelerating action of oxygen, the conversion being 66%, which as about the same magnitude as without oxygen. In a separate experiment catechol was found ineffective in causing the isomerization.

In carbon tetrachloride solution (0.1 c.c. of the ester in 10 c.c.) contained in a tube of a 65 c.c. capacity 23% of the cinnamate was formed by hydrogen bromide (10 c.c.) in four hours. In the same vessel 0.1 c.c. of the allo-cinnamate in 5 c.c. of carbon tetrachloride was isomerized by 5 c.c. of hydrogen bromide in the presence of 20 c.c. of oxygen to the extent of 87% in 22.5 hours and the addition of 25 mg. of catechol reduced the conversion to 62%.

With hydrogen chloride the isomerization took place very slowly and when the reaction temperature was raised to 55°C. it amounted to 14% in the course of 7.5 hours. In carbon tetrachloride under essentially the same conditions as with hydrogen bromide, there was no appreciable formation of the cinnamate with 20 c.c. of hydrogen chloride, whether oxygen was present or not.

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