CII.—*The Action of Bromine Water on Certain Olefinic Acids.*

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IN the course of investigations upon the use of chlorine water and bromine water as effective sources of hypochlorous and hypobromous acids, it has been shown that these reagents react readily with cinnamic, methylcoumaric, and methylcoumarinic acids to form halogenohydrins. In ice-cooled aqueous solutions, at concentrations varying from 0·07*N* to 0·08*N*, and under appropriate conditions, from 95% to 98% of the reacting unsaturated acid was transformed to the chloro- or bromo-hydrin, the remainder giving rise to the corresponding dihalogenide (Read and Andrews, J., 1921, **119**, 1774). Similar results have been recorded for other unsaturated acids by Biilmann (*Rec. trav. chim.*, 1917, **36**, 317), who found that bromine water reacted with fumaric and maleic acids in 0·05*N*-aqueous solutions, forming bromohydrin to the extent of about 96%. Corresponding values for the remaining acids investigated by Biilmann were as follows: crotonic acid (0·05*N*), 100%;

acrylic acid (0·1*N*), 98%; mesaconic acid (0·05*N*), 75%; and itaconic acid (0·1*N*), 68·5%.

During a study of the application of chlorine and bromine water to various types of unsaturated organic substances, we have examined the effect of concentration upon the interaction between bromine water and some of the above olefinic acids and their sodium salts. With maleic acid, 89·3% of the reacting bromine was converted into bromohydrin and hydrobromic acid in a 0·05*N*-aqueous solution, under the conditions adopted; the proportion fell to 81·9% in a 0·10*N*-solution and to 62·5% in a 0·33*N*-solution. Maleic acid thus behaves very similarly to ethylene and allyl alcohol, which appear to be the only unsaturated substances hitherto examined over a range of concentrations in this manner (Read and Hook, J., 1920, **117**, 1214; Read and Hurst, J., 1922, **121**, 989). Sodium maleate, in aqueous solutions of equivalent concentrations, decolorised bromine water with several hundred times the rapidity of free maleic acid; at the same time, the proportions of bromohydrin were distinctly enhanced, and the graph connecting these proportions with the corresponding concentrations became practically rectilinear over the range of concentrations examined. These results are summarised in the appended table :

Percentages of Total Bromine reacting to form Bromohydrin and Hydrobromic Acid.

Maleic acid.		Sodium maleate.		Sodium fumarate.		Itaconic acid.	
N.	%.	*N.*	%.	*N.*	%.	*N.*	%.
0·0500	89·3	0·0500	95·6	—	—	0·0482	96·6
0·0655	87·5	0·0655	95·0	0·0666	96·9	0·0642	96·0
0·1000	81·9	0·1000	92·5	0·1000	95·0	0·0962	94·9
0·1667	74·3	0·1667	87·5	0·2000	89·3	0·1923	89·8
0·3334	62·5	0·3334	75·6	—	—	0·2748	86·3

Interaction between fumaric acid and bromine water was exceedingly slow in the experiments undertaken; sodium fumarate, however, brought about decolorisation with approximately half the speed of sodium maleate, and furnished proportions of bromohydrin slightly higher than those afforded by the latter salt (compare Lossen, *Annalen*, 1906, **348**, 261). Free itaconic acid gave closely similar results, the conversion into bromohydrin being much more complete than in Biilmann's experiments. Coumarin underwent bromination in the benzene nucleus when treated with bromine water, thus resembling methylcoumaric and methylcoumarinic acids (Read and Andrews, *loc. cit.*).

Oleic acid reacted also with bromine water, but in this instance only 51·5% of the bromine was effective in forming bromohydrin at the ordinary temperature, in an approximately decinormal mixture containing some potassium bromide. It was formerly considered essential to conduct the addition of hypochlorous and hypobromous acids to unsaturated compounds in the absence of bright light and at a low temperature; but it has been demonstrated that direct sunlight exerts no apparent influence in the formation of halogenohydrins, according to the methods described, from cinnamic, methylcoumaric, and methylcoumarinic acids (*loc. cit.*), and in the case of ethylene it promotes the reaction (J., 1920, **117**, 1221). An interesting result illustrating the effect of heat was observed in the reaction between indene and bromine water, which appears to be practically unaffected by raising the temperature from 2° to 90° (Read and Hurst, J., 1922, **121**, 2550); we now show, further, that with oleic acid the yield of bromohydrin obtained from fixed weights of the reactants is actually increased when the aqueous emulsion is raised from the ordinary temperature to about 90°. When treated in succession with alcoholic potassium hydroxide and dilute sulphuric acid, the crude product from this last reaction gave a dihydroxystearic acid, m. p. 92—93°. Albitzky (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 76) prepared two stereoisomeric dihydroxystearic acids from the chlorohydrin obtained from either oleic acid or elaidic acid : these melted at 93—95° and 127—128°, respectively. We were unable to attain the melting point, 99—100°, recorded by Saytzeff (*ibid.*, 1892, **24**, 477) and also by Albitzky (*loc. cit.*) for specimens of a dihydroxystearic acid prepared by somewhat different methods.

EXPERIMENTAL.

Maleic Acid.—1. An aqueous solution of maleic acid (10 g. in 250 c.c.) was slowly added at the ordinary temperature to water (500 c.c.) into which a current of air charged with bromine vapour was introduced through a perforated glass bulb (J., 1920, **117**, 359). The liquid was stirred continuously, and the conditions were adjusted so as to maintain an excess of maleic acid in a distinctly yellow solution until no more bromine appeared to be absorbed (16 hours). Unchanged bromine was then removed by passing air through the liquid. The hydrobromic acid formed in the reaction, which was determined titrimetrically, corresponded to the conversion of 26·4% of the maleic acid into bromohydrin; the results given below indicate, however, that the solution contained some unchanged maleic acid. A crystalline deposit of dibromosuccinic acid (2 g., m. p. 255°) separated during the reaction, and a further quantity of this substance was obtained upon concentrating the filtrate.

2. In a further series of experiments, maleic acid was dissolved

in water, together with a molecular proportion of bromine, to form solutions of known concentrations. The mixtures were kept in stoppered flasks at the ordinary temperature in diffused daylight until the bromine was completely absorbed; the amounts of hydrobromic acid produced were then determined in the usual way. The proportions of bromine functioning to form bromohydrin and hydrobromic acid at various concentrations are given in the table on p. 746. Dibromosuccinic acid separated from the solution only in the first of these experiments. In all instances the bulk of the bromine was absorbed within the first 2 days, but complete decolorisation of the solutions took about a week.

Sodium Maleate.—Series (2) above was repeated with the modification that in each case the maleic acid was exactly neutralised with sodium hydroxide before the bromine was added. The bromine was absorbed rapidly, decolorisation being effected within 30 minutes.

Sodium Fumarate.—The interaction between fumaric acid and bromine water was so slow, even under the conditions adopted with success for cinnamic acid (J., 1921, **119**, 1776), that attention was restricted to examining the effect of the reagent on sodium fumarate. The results of a series of experiments, conducted as described in the preceding paragraph, are in the table. Complete absorption of the bromine occupied from 1 to 2 hours.

Itaconic Acid.—When mixed with a molecular proportion of bromine in aqueous solution, itaconic acid reacted much more rapidly than maleic acid, complete decolorisation occurring within an hour under the conditions adopted.

Coumarin.—A solution of coumarin (10 g.) in hot 2*N*-sodium hydroxide (100 c.c.) was diluted with water (750 c.c.) and added drop by drop to ice-water (900 c.c.) containing a little sulphuric acid (2 g.); bromine vapour was simultaneously admitted into the liquid in the usual way, with continuous stirring, for a period of about 5 hours. The viscid syrup obtained by extracting the product with ether gradually deposited small colourless needles when kept; after recrystallisation from alcohol, this substance melted at 159—160°, and was found to be identical with 5-bromocoumarin prepared from 5-bromosalicylaldehyde by Perkin's reaction (compare *Ber.*, 1900, **33**, 2327) (Found: Br, 35·75. Calc. for $C_9H_5O_2Br$: Br, 35·55%). The main product yielded by the coumarin consisted of a viscid liquid with the irritating odour characteristic of halogenohydrins, but no further definite substance was isolated from it. Owing to the occurrence of nuclear substitution, with the formation of hydrobromic acid, the distribution of the bromine could not be ascertained.

Oleic Acid.—To 10 g. of oleic acid, emulsified in 250 c.c. of water at the ordinary temperature, was gradually added a molecular proportion of bromine (5·67 g.) dissolved in aqueous potassium bromide (10 g. in 75 c.c.). The mixture was shaken vigorously throughout the addition. The whole of the bromine was absorbed, and a determination of the resulting hydrobromic acid showed that 51·5% of the halogen had reacted to form this substance and bromohydrin. When the operation was repeated at about 90°, this proportion rose to 57·5%. The ethereal extract yielded in each instance a thick, brown oil, which did not crystallise.

A portion (7·5 g.) of the product from the second experiment was boiled for 2 hours with alcoholic potassium hydroxide (2·5 g. in 90 c.c.); the bulk of the solvent was distilled off, and the residue was heated for an hour on the water-bath with an excess of dilute sulphuric acid. The ethereal extract furnished a syrup from which glistening leaflets (1·2 g., m. p. 92—93°) gradually separated; these appeared to consist of a dihydroxystearic acid (Found: C, 68·0; H, 11·1. $C_{18}H_{36}O_4$ requires C, 68·35; H, 11·4%).

Related investigations are in progress.

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