

CCCV.—*The Action of Bromine Water on Indene.*

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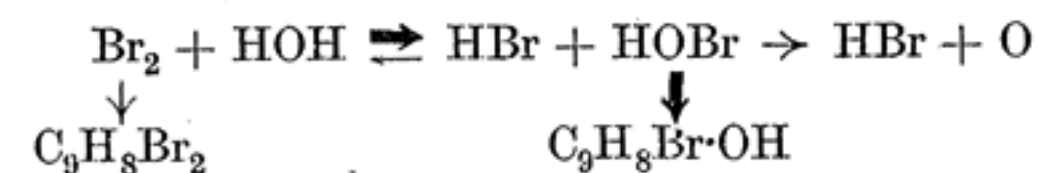
IN a series of communications dealing with the action of chlorine water and bromine water on unsaturated substances, it has been shown that these reagents function with unsuspected ease as sources of potential hypochlorous and hypobromous acids. In the case of ethylene (T., 1917, 111, 240; 1920, 117, 359, 1214), owing to the gaseous nature and slight solubility of the hydrocarbon, the reaction is comparatively slow, and, in accordance with the generally accepted view, the formation of halogenohydrin is promoted by cooling. The similar but much more rapid reactions which lead to the formation of halogenohydrins from cinnamic acid and certain substituted cinnamic acids (T., 1921, 119, 1774) and from allyl alcohol (this vol., p. 989) likewise yield the most satisfactory results at low temperatures. These observations might therefore be correlated with the tendency of hypochlorous and hypobromous acids to undergo decomposition when heated in dilute aqueous solution. Such decomposition, however, appears also to be accelerated by sunlight, whereas in no instance in this series of investigations has sunlight proved detrimental to halogenohydrin formation; the formation of ethylenebromohydrin, indeed, appears to be promoted by conducting the reaction in bright sunlight (*loc. cit.*, p. 1221).

It was thus of particular interest to discern, in the interaction between bromine water and indene, an instance of halogenohydrin formation which appeared to be promoted by the application of heat. The bromohydrin in question, 2-bromo-1-hydroxyhydrindene, was originally prepared in very unsatisfactory yield by the prolonged action of boiling aqueous alcohol on dibromohydrindene (Krämer and Spilker, *Ber.*, 1890, 23, 3276). Later, in utilising this substance for the preparation of 1-hydroxy-2-hydrindamine, Pope and Read (T., 1912, 101, 760) showed that it could be obtained rapidly, in 85 per cent. yield, by adding bromine, dissolved in potassium bromide solution, to an emulsion of indene in hot water, whilst in the presence of cold water the yield declined to 70 per cent. (T., 1911, 99, 2072).

When the reaction between bromine water and indene was submitted to a careful quantitative examination, according to the general method described in previous communications, considerable difficulty was experienced in obtaining trustworthy data at the lower temperatures owing to the formation of pasty aggregates consisting of the reaction products mixed with unchanged indene. On overcoming this difficulty by the addition of kieselguhr to the reaction mixture, a practically quantitative conversion of indene to the bromohydrin

occurred at the ordinary temperature, and no appreciable difference was observed when the reaction was carried out at 90°. The discrepancy to which reference has been made is thus to be ascribed to incomplete reaction, caused by defective admixture at the lower temperature, and the conclusion is reached that the reaction between bromine water and indene is not appreciably affected by raising the temperature to 90°. In view of the sensitiveness to heat and light of dilute aqueous solutions of hypobromous acid, it is very remarkable that bromine water when functioning as a source of potential hypobromous acid should be capable of exhibiting such indifference to either of these influences. That the reaction involves an intermediate formation of dibromide is unlikely, considering the resistance of dibromohydrindene to partial hydrolysis (*v. supra*).

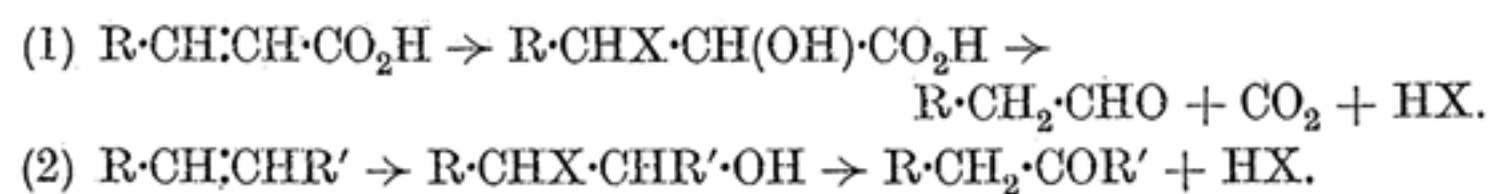
Owing, first, to the common instability of halogenohydrins in contact with hot dilute acid, and, secondly, to the oxidative action of warm aqueous solutions of chlorine and bromine, considerable difficulty exists in studying the addition of hypochlorous and hypobromous acids to unsaturated substances by the use of hot chlorine water or bromine water; it is hoped, however, to investigate other instances in which the halogenohydrin, like the bromohydrin of indene, is stable under the conditions mentioned. The evidence now available leads to the suggestion that even at high temperatures and in the presence of sunlight the velocity of halogenohydrin formation is much greater than the velocity of decomposition of hypochlorous or hypobromous acid. The complete scheme of reaction for indene and bromine water is summarised in the appended diagram, the only processes which occur to any appreciable extent being indicated by the thick arrows:



Preliminary attempts to utilise chlorine water as a source of potential hypochlorous acid in a similar reaction were unsuccessful, owing to the ready conversion of indene to tarry matter under the conditions adopted. It is of interest, however, that indene combines readily with hypochlorous acid, a 77 per cent. yield of chlorohydroxyhydrindene having been obtained by this method (Weissgerber, *Ber.*, 1911, 44, 1443).

Attention has already been directed (T., 1921, 119, 1775) to the very convenient method which is available for the preparation, in excellent yield, of phenylacetaldehyde from cinnamic acid by the successive action of chlorine water and aqueous alkali and acid. In a like manner, β -hydrindone is easily accessible from indene by suc-

cessive treatment with bromine water, alcoholic alkali, and dilute acid. The two general methods involved in these operations are summarised in the following schemes of reaction :



Heusler and Schieffer (*Ber.*, 1899, **32**, 30) have directed attention to the very reactive nature of the halogen in chlorohydroxyhydrindene, the monomethyl ether of hydrindene glycol being produced by warming the substance with alcoholic sodium methoxide; in the case of bromohydroxyhydrindene the corresponding monoethyl ether was produced on treatment with warm alcoholic sodium ethoxide, and this derivative underwent hydrolysis with hot dilute sulphuric acid, yielding β -hydrindone. The final treatment with acid was found to be desirable even when the hydrolysis was effected by means of a slight excess of alcoholic potassium hydroxide.

EXPERIMENTAL.

The Interaction between Cold Bromine Water and Indene.—(1) Indene was added in portions of 5 grams to 1000 c.c. of water, the mixture being cooled to about 2° and submitted to vigorous mechanical stirring throughout the experiment. A slow current of air charged with bromine vapour was passed into the liquid until the attainment of a permanent pale yellow tint, whereupon a titrimetric estimation was made of the amount of hydrobromic acid contained in an aliquot part of the aqueous liquid, in accordance with the principle outlined in previous communications. The process was repeated until 20 grams of indene had been added, the progress of the reaction being ascertained by titration at the end of each stage. Towards the end of the experiment the absorption of bromine was slow, owing to the formation of a pasty mass containing unchanged indene. The titration values fluctuated considerably, and indicated yields of bromohydrin varying from 50 to 70 per cent. of the amounts theoretically possible. By washing the pasty product with light petroleum, the solid bromohydrin was obtained in an almost pure condition; after two recrystallisations from methylated spirit, it melted at 130° (Found: Br = 37.7. $\text{C}_9\text{H}_9\text{OBr}$ requires Br = 37.5 per cent.). The petroleum washings contained unchanged indene together with a heavy oil, which was reserved for further examination.

(2) A similar experiment was carried out with the addition of light petroleum, the titration values being corrected in accordance with the results of a control experiment which indicated a slight

absorption of bromine by the petroleum under the experimental conditions. The formation of a semi-solid mass was prevented by the petroleum, and the titration results corresponded with yields of bromohydrin varying from 75 to 85 per cent. of the amounts theoretically possible. The petroleum, on evaporation, yielded a small quantity of a heavy oil; this contained dibromohydrindene, which was probably formed largely as a result of reaction in the petroleum phase.

(3) The experiment was repeated, with the substitution of kieselguhr (10 grams) for light petroleum. Ready absorption of bromine occurred, and the titrimetric estimations indicated an almost complete conversion of indene to bromohydrin; the mean value being 98 per cent. The actual weight of the solid product collected was about 90 per cent. of the theoretical yield.

The Interaction between Bromine Water and Indene at 90° .—Six distinct experiments were performed, each dealing with a different concentration of indene, the procedure being in each instance as follows :

To 1000 c.c. of water, maintained at 90° , was added in one portion a known weight of indene (5, 10, 15, 20, 30, and 40 grams). To the mixture, thoroughly emulsified by vigorous shaking, a 7 per cent. solution of bromine in aqueous potassium bromide was added with moderate rapidity until the attainment, after continued shaking, of a permanent pale yellow tint. A considerable quantity of the resulting bromohydrin remained in solution at 90° , and crystallised in long, colourless needles on cooling; the remainder of the solid product formed hard but somewhat sticky aggregates. The aqueous filtrate and washings were freed from traces of bromine by the passage of a rapid air current, after which an aliquot portion was titrated with standard sodium bicarbonate solution. The yields of bromohydrin corresponding with the titration results varied from 98.5 to 100 per cent. of the amounts theoretically possible, the mean value being 99 per cent.

A preliminary control experiment showed that the amount of hydrobromic acid formed, in the absence of indene, under the conditions adopted was so small as to be negligible. That the high titration values were not due to decomposition of hypobromous acid or hydrolysis of the bromohydrin is also evident from the fact that between 90 and 95 per cent. of the calculated yield of the solid compound was actually collected in the six experiments described.

Subsidiary Products of the Reaction.—The various preparations of bromohydroxyhydrindene were united (480 grams) and recrystallised carefully, in an attempt to isolate the second externally

compensated form of the substance which is theoretically possible. The main product of the reaction, after recrystallisation from alcohol, melted at 130° , and the final mother-liquors yielded a small amount of an oil, the bulk of which distilled at $130\text{--}165^{\circ}/18$ mm. (34 grams). The distillate contained 39.8 per cent. of combined bromine, and appeared to consist essentially of bromohydroxyhydrindene ($\text{C}_9\text{H}_9\text{OBr}$ requires $\text{Br} = 37.5$ per cent.). After keeping for several weeks, the oil, which possessed a very irritating odour, deposited crystals; these, when separated from adhering mother-liquor, showed an ill-defined melting point, pronounced softening occurring at about 85° . The material was extremely soluble in most of the usual organic solvents, from which it was deposited as an oil. The evidence thus appears to indicate the formation of a small amount of an isomeric bromohydrin of low melting point and high solubility. Similar observations have been recorded in the cinnamic acid series (*loc. cit.*, p. 1776).

The light petroleum washings of the original semi-solid separations also yielded a similar oily product, the major portion of which distilled at $135\text{--}160^{\circ}/18$ mm. The percentage of bromine (49.1) corresponded in this instance with a mixture of dibromide and bromohydrin.

The Conversion of Bromohydroxyhydrindene to β -Hydrindone.—Bromohydroxyhydrindene was heated under reflux for half an hour with a 4 per cent. alcoholic solution of potassium hydroxide (slightly more than one equiv.). The bulk of the alcohol was then removed and the residue again heated under reflux with an excess of dilute sulphuric acid. On steam distilling the product, the ketone was readily obtained as a colourless, crystalline mass, in about 75 per cent. yield. It separated from dilute alcohol in long, silky needles having a very faint yellow tinge. After several weeks, the crystals became yellow and somewhat pasty. The melting point of the freshly recrystallised substance was 58° ; this result agrees with the observations of Schad (*Ber.*, 1893, 26, 222) and Heusler and Schieffer (*loc. cit.*), the value 61° recorded by Benedict and Wislicenus (*Annalen*, 1893, 275, 352) being doubtlessly too high.