

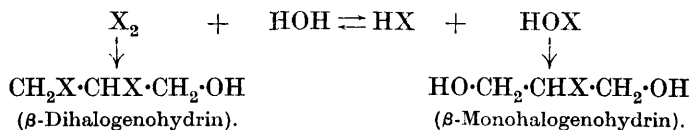
## CXVII.—*The Conversion of Allyl Alcohol to Glyceryl Chloro- and Bromo-hydrins.*

By JOHN READ and ERIC HURST.

It is remarkable that, in spite of their early discovery and manifold applications, the chloro- and bromo-hydrins derived from glycerol are even yet by no means accurately known. A reference to the literature indicates, indeed, the existence of considerable uncertainty in regard to these derivatives (see, for instance, Beilstein, "Handbuch der organischen Chemie," 4th ed., 1920, I, 477). Even in the case of the readily accessible  $\beta$ -dibromohydrin, no trustworthy determination of density appears to have been made until comparatively recently (Forster and Withers, T., 1912, **101**, 496; Philip, T., 1912, **101**, 1868). As has already been indicated in references to other halogenohydrins (T., 1920, **117**, 1214; 1921, **119**, 1774), this position is largely due to the nature of the methods which have hitherto been utilised in preparing such substances. Like ethylenebromohydrin, the derivatives now under discussion have usually been prepared from the corresponding polyhydric alcohol by interaction with (1) the anhydrous halogen acid, or (2) a phosphorus haloid; the enhanced difficulty, in the case of a trihydric alcohol, of controlling such reactions so as to yield a well-defined product is manifest. Thus (1), Berthelot (*Ann. Chim.*, 1861, [iii], **61**, 296) prepared  $\alpha$ -monochlorohydrin by the interaction of glycerol and hydrogen chloride at 100°, whilst Hanriot (*Ann. Chim.*, 1879, [v], **17**, 73) stated that the product contained a small proportion of  $\beta$ -monochlorohydrin which could be separated by fractional distillation under diminished pressure, the boiling points being 139°/18 mm. ( $\alpha$ ) and 146°/18 mm. ( $\beta$ ). More recently, Nivière (*Compt. rend.*, 1913, **156**, 1628) prepared  $\alpha$ -monochlorohydrin (b. p. 121·5—122·5°/15 mm.) by saturating glycerol with hydrogen chloride at 120—130°. The same reagents have also been used in preparing  $\alpha$ - and  $\beta$ -dichlorohydrin (Fauconnier, *Bull. Soc. chim.*, 1888, [ii], **50**, 212). Further (2), Berthelot and de Luca (*Ann. Chim.*, 1856, [iii], **48**, 304) found that chlorides of phosphorus reacted with glycerol to give a mixture of mono- and di-chlorohydrins and epichlorohydrin, together with large amounts of other products. Similar methods have been applied in preparing the corresponding bromohydrins (Berthelot and de Luca, *loc. cit.*; Carré, *Bull. Soc. chim.*, 1910, [iv], **7**, 835).

Another principle (3), namely, that of direct addition of hypochlorous or hypobromous acid to a suitable unsaturated substance, has been utilised to some extent in other investigations of the kind

under notice. Henry (*Ber.*, 1870, **3**, 351; 1872, **5**, 449; *Rec. trav. chim.*, 1897, **16**, 208) stated that allyl derivatives combined readily with hypochlorous acid, but that in the case of allyl alcohol the yield of  $\beta$ -monochlorohydrin was small, owing apparently to oxidation. The successful results which have attended the use of chlorine water and bromine water in the preparation of halogenohydrins from unsaturated substances (T., 1917, **111**, 240; 1920, **117**, 359, 1214; 1921, **119**, 1774) led us to apply these reagents to allyl alcohol under the customary conditions. In accordance with the general principle which has been laid down for the mobile equilibrium involved, the product should consist of a mixture of monohalogeno- and dihalogeno-hydrin, resulting from the simultaneous occurrence of the two additive reactions indicated below:



From observations made in the study of similar processes of this type, it seemed likely that the main product of the reaction would be  $\beta$ -monohalogenohydrin (compare Henry, *loc. cit.*), and that the separation of this derivative from the accompanying  $\beta$ -dihalogenohydrin would be simple in comparison with the treatment of the complex mixtures which result from glycerol by the application of principles (1) or (2).

Apparently the action of chlorine water on allyl alcohol has not been investigated hitherto, but its bromination in aqueous solution was undertaken by Markownikoff (*Jahresber.*, 1864, 490) for the preparation of  $\beta$ -dibromohydrin ( $\beta$ -dibromopropyl alcohol). Subsequently, Fink (*Monatsh.*, 1887, **8**, 562) showed that addition of hypobromous acid occurred in the reaction, and that as much as 45 per cent. of the bromine could be converted to hydrobromic acid. The reaction, which was more fully studied by Biilmann (*J. pr. Chem.*, 1900, [ii], **61**, 215), appears to be the only one on record, prior to the present series of investigations, in which the possibility was recognised of bromine water functioning effectively as a source of hypobromous acid.

The results of the experiments now described were such as to confirm the above-mentioned anticipations, but with chlorine water the process was complicated by the simultaneous occurrence of other reactions. In the case of bromine water, the results stand in close correspondence with those given by ethylene (T., 1920, **117**, 1214). The reactions thus yielded specimens of four definite halogenohydrins: namely,  $\beta$ -monochlorohydrin,  $\beta$ -dichlorohydrin,

$\beta$ -monobromohydrin, and  $\beta$ -dibromohydrin. With the exception of  $\beta$ -dichlorohydrin, these appeared to be chemically pure, and in the majority of instances the observed physical constants, when compared with the somewhat scanty data at our disposal, were in agreement with this conclusion. For the preparation of the pure  $\beta$ -dihalogenohydrins, the halogenation of allyl alcohol in carbon disulphide solution, in the manner devised by Tollens (*Annalen*, 1870, **156**, 166; 1873, **167**, 224) and improved by Kohler (*Amer. Chem. J.*, 1909, **42**, 381), is to be recommended; but when the  $\beta$ -monohalogenohydrin is also required, the reactions now described should be of practical importance, particularly in preparing the bromine derivatives.

#### EXPERIMENTAL.

##### *The Reaction between Allyl Alcohol and Bromine Water.*

A large beaker, surrounded with melting ice and provided with a mechanical stirring apparatus, was charged with a solution of allyl alcohol (about 10 grams) in water (about 600 c.c.). On passing a current of air laden with bromine vapour into the well-stirred liquid, in the manner already described for ethylene (T., 1920, **117**, 359), absorption occurred with extreme rapidity. The operation was continued until the attainment of a permanent pale yellow tint. The volume of the reaction mixture was then noted, after which a small measured volume (5 or 10 c.c.) was withdrawn and diluted with water. The slight excess of bromine was removed by aspirating air through the solution, and the hydrobromic acid present was then determined by titration with standard silver nitrate solution, control experiments having indicated absence of hydrolysis of the dissolved bromohydrins under the conditions adopted. The total amount of bromine passed into the liquid was determined by weighing the receptacle containing this reagent before and after the operation. The two values obtained as stated were utilised to calculate the distribution of bromine in the reaction; the amounts of bromine used stood in satisfactory agreement with the corresponding weights of allyl alcohol, when pure anhydrous preparations were used.

Further successive portions of allyl alcohol were then introduced into the reaction vessel, the various determinations being repeated on each occasion. The appended table contains a summary of the results obtained in one such series of experiments. The calculations take into account the changes of volume which occurred throughout the process, but no correction is made for the very slight loss of bromine by diffusion. The temperature of the solution varied from 1.5° to 3.5°, and the operations were conducted in diffused daylight.

Towards the end of the third stage a second phase appeared, and from this point onwards the lower layer, which consisted mainly of  $\beta$ -dibromohydrin, gradually increased in bulk.

Stage.	Total bromine present (grams).	Total bromine present as $C_3H_5(OH)_2Br + HBr$ (grams).	Percentage of total bromine reacting to form $C_3H_5(OH)_2Br + HBr$ .	Concentration of $C_3H_5(OH)_2Br$ .	
				Grams per litre.	Normality.
1	23.5	20.38	86.7	32.4	0.209
2	45.5	38.16	83.9	58.8	0.379
3	67.5	53.48	79.2	81.1	0.523
4	89.5	68.54	76.6	103.9	0.670
5	111.7	81.82	73.2	123.0	0.794
6	133.7	94.38	70.6	140.8	0.908
7	156.2	107.14	68.6	157.5	1.016

From these results it is evident that the mobile equilibrium already referred to suffers displacement towards the left as the reaction progresses and the products accumulate in the solution. The monobromohydrin : dibromohydrin ratio thus declines from 6.5 : 1 at the beginning of the series to 2.2 : 1 at the end. As in the case of ethylene, this result is probably due in part to the difference in solubility between the monobromohydrin and the dibromohydrin; the concentration of the latter product in the solution is thus kept relatively low by its separation as a distinct phase during the early part of the reaction, whilst the concentration of the monobromohydrin increases throughout a considerably longer period.

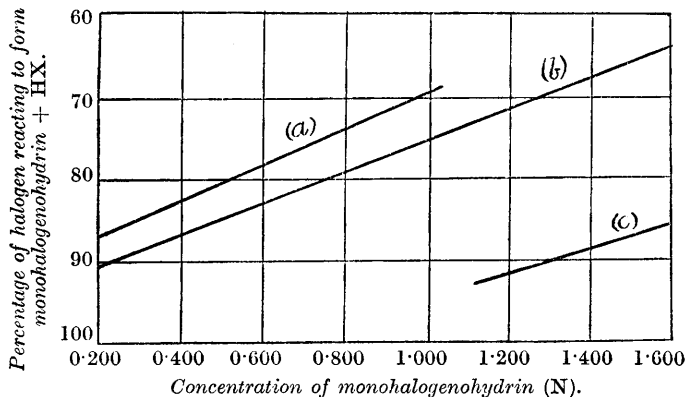
When the concentrations of monobromohydrin, as expressed by the normality factor ( $x$ ), are plotted against the corresponding percentages of bromine functioning as hypobromous and hydrobromic acids ( $y$ ), a regular curve is obtained [Fig. 1 (*a*)]; this approximates to a straight line, and is closely defined by the equation :  $y = 91.5 - 22.9x$ . The diagram (Fig. 1) illustrates the essential similarity of the reactions between (*a*) bromine water and allyl alcohol, (*b*) bromine water and ethylene (T., 1920, **117**, 1219), and (*c*) chlorine water and ethylene (Gomberg, *J. Amer. Chem. Soc.*, 1919, **41**, 1420). It is interesting to note that the halogenohydrin : dihalogenide ratio at corresponding concentrations increases from (*a*) to (*c*).

$\beta$ -Monobromohydrin,  $OH \cdot CH_2 \cdot CHBr \cdot CH_2 \cdot OH$ .—For the preparation of  $\beta$ -monobromohydrin, the reaction just described may conveniently be prolonged until the concentration of this substance in the solution has reached 1.0*N* to 1.25*N*, as disclosed by titration. The amount of monobromohydrin thus produced accordingly reaches about 60 per cent. of the theoretical yield. Although formed readily and in very satisfactory yield by this

method, the isolation of the monobromohydrin from the aqueous liquid and its subsequent separation from the accompanying dibromohydrin in a state of purity presented appreciable difficulty. This result was due mainly to the instability of the monobromohydrin when distilled repeatedly under diminished pressure; it must also be attributed partly to incomplete extraction of the substance from the original aqueous solution.

The extraction was in all cases accomplished after careful neutralisation of the ice-cooled solution with powdered sodium carbonate. Fairly satisfactory results were achieved by a threefold extraction with ether after saturation with sodium chloride, or, better, with anhydrous sodium sulphate, at the ordinary temperature. A similar extraction with acetone after saturation with calcium

FIG. 1.



chloride gave a somewhat higher yield. The best result was reached by saturating the solution with anhydrous sodium sulphate at 30° and extracting it with three successive quantities of ether; in this way the extraction attained an efficiency of about 70 per cent.

The ether extract, when dried over sodium sulphate and distilled from the water-bath, left a pale brown oil consisting of a mixture of the mono- and di-bromohydrins. The composition of this and all other similar mixtures examined in the course of the investigation was ascertained by alkaline hydrolysis, followed by a volumetric determination of bromide in the product. Control experiments demonstrated that mono- and di-bromohydrins are quantitatively hydrolysed when boiled for two hours under reflux with excess of aqueous potassium hydroxide.

In a particular preparation, the oily residue obtained from the ether extract, after being freed from ether by the passage of a rapid current of air, contained 61.2 per cent. of bromine. This result

corresponded with a mixture of 56.0 per cent. of monobromohydrin (Br = 51.6 per cent.) and 44.0 per cent. of dibromohydrin (Br = 73.4 per cent.). According to the titration of the original aqueous solution, 62 per cent. of the bromine had reacted to form monobromohydrin and hydrogen bromide; it follows, therefore, that the extraction of the dibromohydrin was somewhat more efficient than that of the more soluble monobromohydrin.

In all, 510 grams of oil were prepared, having characteristics agreeing closely with those of the preparation to which reference has just been made. The isolation of the two constituents was accomplished by continued fractional distillation under a pressure of about 20 mm. The oil, which was neutral to litmus, was distilled in portions from a Claisen flask fitted with a short fractionating column and heated by means of an oil-bath. The progress of the separation was followed by means of the bromine values of the fractions, corrections being applied, when necessary, for small amounts of hydrogen bromide formed during the process. It was found that the monobromohydrin, which is the constituent of higher boiling point, underwent a slow polymerisation, or analogous change, during the distillation. Consequently, after the six distillations which were undertaken in the attempt to prepare chemically pure products, only a small quantity of the monobromohydrin was obtained, the bulk of the substance having been transformed partly into a less volatile liquid, distilling over an indefinite range of temperature, and partly into a thick black tar. By curtailing the number of distillations, a much higher yield of only slightly impure  $\beta$ -monobromohydrin could be secured.

The following table, in which are embodied the results of the third fractional distillation of the above series, indicates the way in which the separation proceeds:

Fraction.	Range of fraction.	Weight of fraction (grams).	Percentage of combined bromine.	Percentage of $C_3H_5(OH)_2Br$ .	Percentage of $C_3H_5(OH)Br_2$ .
1	90—112°	15.5	41.5	—	—
2	112—116	82.0	71.9	7.0	93.0
3	116—118	143.3	70.8	11.8	88.2
4	118—125	43.0	69.9	16.0	84.0
5	125—135	32.3	62.6	49.4	50.6
6	135—140	17.5	56.7	76.7	23.3
7	140—143	23.1	51.1	100	—

Residue and loss during distillation, 65.8 grams.

During the course of the distillations it was noticed that fractions of fairly constant boiling point, and giving analytical results corresponding closely with (a) monobromohydrin, and (b) dibromohydrin, respectively, tended to distil in the neighbourhood of

(a)  $140^{\circ}/20$  mm., and (b)  $110^{\circ}/20$  mm. The two kinds of fractions indicated were accumulated until the end of the fifth fractionation, when it appeared of little use to prolong the process. Accordingly, each of the fractions in question was submitted to a final fractionation. The monobromohydrin fraction, which weighed 55 grams, nearly all distilled at  $136\text{--}138^{\circ}/21$  mm., and on alkaline hydrolysis gave 51.6 per cent. of bromine ( $\text{C}_3\text{H}_7\text{O}_2\text{Br}$  requires  $\text{Br} = 51.6$  per cent.). It was thus regarded as chemically pure  $\beta$ -monobromohydrin. The dibromohydrin fraction, which weighed 210 grams, distilled completely at  $111\text{--}114^{\circ}/20$  mm., and contained 72.8 per cent. of bromine ( $\text{C}_3\text{H}_6\text{OBr}_2$  requires  $\text{Br} = 73.4$  per cent.). Thus, of the dibromohydrin present in the original 510 grams of crude product, about 90 per cent. was isolated in a state of purity; whilst of the monobromohydrin not quite 20 per cent. was isolated.

The  $\beta$ -monobromohydrin thus obtained was a colourless and very viscous liquid. On keeping for some time, it developed a pale yellow colour. Its vapour had an irritant action similar to that of ethylenebromohydrin (T., 1920, 117, 1221). It was miscible with alcohol, acetone, or ether, but only partly miscible with benzene at the ordinary temperature. A determination of density gave  $d_4^{20}$  1.7858 (vacuum). It is of interest that the calculated ratio of its molecular radius to that of water (Holmes, T., 1913, 103, 2147) is 1.69.  $\beta$ -Monobromohydrin thus occupies a position between nicotine (1.65) and phenol (1.70) in Holmes's table (*loc. cit.*, p. 2164); like  $\beta$ -monochlorohydrin (*v. infra*), it thus appears to stand on the border line between miscible and partly miscible liquids. When gradually diluted with water at the ordinary temperature, complete miscibility occurred over a certain range; further dilution produced a turbidity which persisted until a relatively large volume of water had been added.

$\beta$ -Dibromohydrin,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OH}$ .—As already indicated, the foregoing method, although designed primarily for the production of  $\beta$ -monobromohydrin, led simultaneously to the isolation of comparatively large amounts of  $\beta$ -dibromohydrin. Further investigations were carried out with the object of modifying the method so as to promote the formation of dibromohydrin and to facilitate its separation from the reaction mixture. In accordance with these aims, the proportion of water used in the preparation was considerably reduced.

A solution of allyl alcohol in its own weight of water was cooled by immersion in melting ice and vigorously stirred. Liquid bromine was then added slowly from a burette. Rapid reaction occurred, and a heavy oily phase soon separated. At the end of the addition, the mixture was neutralised in the cold with powdered sodium



carbonate, and then saturated at the ordinary temperature with anhydrous sodium sulphate. The oily layer was then separated and dried with the same agent. Mixed preparations made in this way, amounting to 350 grams, contained 67·5 per cent. of bromine. Since there was no evidence of subsidiary reactions having taken place, this result indicated the presence of 72·9 per cent. of dibromohydrin and 27·1 per cent. of monobromohydrin in the oil. The weight of oil isolated in this very simple way was about 88 per cent. of the calculated amount. The extraction was therefore decidedly more efficient than in the preceding method, whilst the proportion of dibromohydrin in the mixture was almost double the former amount. It may be added that this ratio was confirmed by titrimetric estimations of the hydrogen bromide produced in the reaction, the percentage of bromine reacting to form dibromohydrin in two such experiments being 70·7 and 74·1, respectively.

Purification of the dibromohydrin was effected by repeated fractional distillation from a Claisen flask provided with a short fractionating column, the process being controlled by observation of boiling points and analysis of the fractions, in the manner already described. After three fractionations, a yield of 223 grams of dibromohydrin was obtained, boiling at 111–114°/20 mm., and giving 72·1 per cent. of bromine on alkaline hydrolysis ( $\text{C}_3\text{H}_6\text{OBr}_2$  requires  $\text{Br} = 73\cdot4$  per cent.). The preparation was therefore not quite as pure as the first one described, which had been fractionally distilled six times. The above yield amounts to 87 per cent. of the dibromohydrin present in the crude oil; when referred to the weight of allyl alcohol used, it corresponds with about 50 per cent. of the weight of dibromohydrin theoretically possible.

$\beta$ -Dibromohydrin is a heavy liquid with an irritating odour. It is less viscous than  $\beta$ -monobromohydrin, and it remains colourless when kept. It is miscible with ether, alcohol, or acetone, and also with benzene; in the last respect it differs from  $\beta$ -monobromohydrin. It is only slightly soluble in water at the ordinary temperature. The density of the purer specimen noted above ( $\text{Br} = 72\cdot8$  per cent.) was determined as  $d_4^{20^\circ} 2\cdot1197$  (vacuum); the Holmes value is thus 1·79. The second preparation described ( $\text{Br} = 72\cdot1$  per cent.) gave  $d_4^{20^\circ} 2\cdot1019$ . A specimen of Kahlbaum's  $\beta$ -dibromohydrin contained only 70·2 per cent. of bromine, and had  $d_4^{20^\circ} 2\cdot0897$ .

#### *The Reaction between Allyl Alcohol and Chlorine Water.*

A preliminary control experiment showed that when chlorine is passed into ice-cooled water in diffused daylight the amount of hydrochloric acid produced is so small as to be negligible in titrimetric estimations of the kind described in this paper. Accordingly,



the action of cold dilute chlorine water on allyl alcohol was studied in the manner adopted for bromine water, the allyl alcohol being added in seven or eight portions of about 10 grams to a volume of water originally measuring 600 c.c. Very ready reaction ensued, but the results of the quantitative estimations failed to exhibit the marked regularity observed in the case of bromine. The following summary indicates that the apparent monochlorohydrin : dichlorohydrin ratio fluctuated somewhat at the beginning of the reaction and then declined very slowly. Owing to the vigour of the reaction it seemed likely that these results were influenced considerably by the occurrence of subsidiary reactions; this inference was borne out by an analysis of the quantitative data obtained in several series of experiments.

Stage.	Percentage of total chlorine reacting to form		Stage.	Percentage of total chlorine reacting to form	
	$\text{C}_3\text{H}_5(\text{OH})_2\text{Cl}$ + $\text{HCl}$ .	Normality of $\text{C}_3\text{H}_5(\text{OH})_2\text{Cl}$ .		$\text{C}_3\text{H}_5(\text{OH})_2\text{Cl}$ + $\text{HCl}$ .	Normality of $\text{C}_3\text{H}_5(\text{OH})_2\text{Cl}$ .
1	78.4	0.189	5	75.3	0.953
2	81.4	0.361	6	74.5	1.088
3	79.4	0.528	7	74.9	1.208
4	79.1	0.678			

With 50 per cent. aqueous solutions of allyl alcohol, reaction occurred so vigorously that even with very efficient cooling and stirring it was found necessary to pass the chlorine very slowly and to dilute it with air. During the process the liquid became yellow and formed two liquid phases, but these usually reverted to a homogeneous solution on completion of the reaction. The various preparations, made in the two ways indicated, when united amounted to 594 grams; the product contained 35.05 per cent. of chlorine, as shown by alkaline hydrolysis, and hence the apparent proportion of monochlorohydrin present was 87.1 per cent. After a series of eight systematic fractional distillations under diminished pressure, conducted and controlled in the manner already explained for the corresponding bromine derivatives, it appeared that the mixture contained, not only the two chlorohydrins anticipated, but also appreciable quantities of materials of lower and higher boiling points. The characteristics of the main fractions ultimately obtained are summarised in the appended table :

Fraction.	Boiling point.	Pressure (mm.).	Weight of fraction (grams).	Percentage of chlorine.
1	81—81.5°	13.5	104.3	52.6
2	122.5—123.5	13.5	86.4	31.6
3	125—198	13.5	59.3	33.3

( $\text{C}_3\text{H}_5\text{OCl}_2$  requires  $\text{Cl} = 55.0$ ;  $\text{C}_3\text{H}_7\text{O}_2\text{Cl}$  requires  $\text{Cl} = 32.1$  per cent.).

In accordance with their constant boiling points and general properties, fractions 1 and 2 were regarded as consisting of  $\beta$ -dichloro- and  $\beta$ -monochloro-hydrin, respectively, although it is to be noted that the chlorine value, determined by hydrolysis with aqueous alkali, was somewhat low in the former instance. Alkaline hydrolysis in alcoholic solution gave an almost identical result, which was also confirmed by the method of Carius. The yields of dichlorohydrin calculated on the weights of (a) allyl alcohol, and (b) crude oil are (a) 11.2 and (b) 17.6 per cent., respectively. The corresponding yields of monochlorohydrin are (a) 10.8 and (b) 14.5 per cent. The united yields of monochlorohydrin and dichlorohydrin are, therefore, (a) 22.0 and (b) 32.1 per cent.

It is thus apparent that although the action of chlorine water on allyl alcohol leads to the production of  $\beta$ -monochlorohydrin and  $\beta$ -dichlorohydrin, the yields of these two substances are low and their separation in a state of purity is difficult. This result must be attributed in large measure to the vigour of the reaction, which entails the conversion of a high proportion of the allyl alcohol into other products.

*$\beta$ -Monochlorohydrin*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$ . —  $\beta$ -Monochlorohydrin, prepared in the manner just described, was a colourless and very viscous liquid, possessing a marked irritating odour and boiling at  $122.5\text{--}123.5^\circ/13.5\text{ mm.}$  When kept for some time it became pale yellow. It was miscible with alcohol, ether, or acetone, but only partly miscible with benzene. Determinations of density gave  $d_4^{20}$  1.3416 and  $d_4^{20}$  1.3241 (vacuum). The ratio of the molecular radius to that of water is thus 1.67. When diluted with water at the ordinary temperature,  $\beta$ -monochlorohydrin behaved similarly to  $\beta$ -monobromohydrin. It is to be noted that the observations now recorded differ from the statements of other investigators to the effect that  $\beta$ -monochlorohydrin and  $\beta$ -monobromohydrin are completely miscible with water (compare Henry, *loc. cit.*, and Biilmann, *loc. cit.*). In the case of ethylenebromohydrin the difficulty of eliminating the last traces of the non-miscible dibromide was described in a former paper (*loc. cit.*, p. 1216); but although similar difficulties exist in these instances, the monohalogenohydrins clearly approach the region of partial miscibility in Holmes's table. The glyceryl monobromohydrin described by Veley (*Jahresber.*, 1883, 858) is stated to be immiscible with water (b. p.  $160^\circ/60\text{ mm.}$ ,  $d_4^{20}$  1.717), whilst the supposed glyceryl monobromohydrin of Wohl and Neuberg, obtained in small yield by the action of calcium hypobromite and boric acid on allyl alcohol (*Ber.*, 1899, 32, 3490), was crystallised from aqueous solution (m. p.  $227\text{--}230^\circ$ ).

Fraction 3 in the above table, boiling indefinitely at 125—198°/13.5 mm., possessed similar solubility relationships, but its density was appreciably higher:  $d_4^{20}$  1.3571;  $d_4^{20}$  1.3382 (vacuum). The fraction would thus appear to contain an isomeric monochlorohydrin, and in mentioning this possibility attention may be directed to the reported occurrence of several unexpected isomeric monobromohydrins, including the curious solid compound prepared by Wohl and Neuberg (*loc. cit.*).

$\beta$ -Dichlorohydrin,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$ .—The specimen of  $\beta$ -dichlorohydrin described above was colourless and less viscid than  $\beta$ -monochlorohydrin, and it developed no yellow colour on keeping. It distilled very regularly at 81—81.5°/13.5 mm. It was miscible with alcohol, ether, or acetone, and also with benzene, but was only slightly soluble in water at the ordinary temperature. Two determinations of density were made:  $d_4^{20}$  1.3745;  $d_4^{20}$  1.3534 (vacuum). The Holmes ratio, calculated from the latter value, is 1.74.

### Summary.

1. Cold chlorine water and bromine water have been shown to react with allyl alcohol to produce in each instance glyceryl  $\beta$ -monohalogeno- and  $\beta$ -dihalogeno-hydrin, the former in predominating amount.

2. With chlorine water, the process is difficult to control, and much of the allyl alcohol is converted to other products; but with bromine water the reaction pursues a course parallel to that between bromine water and ethylene, and should be of practical importance as a preparative method.

3. The physical characteristics of the four halogenohydrins thus prepared are summarised in the following table and compared with the corresponding data available for other preparations of these substances:

Substance.	Boiling point.		$d_4^{20}$ .	
	Observed.	Recorded.	Observed.	Recorded.
$\beta$ -Monochloro-hydrin	122.5—123.5°/ 13.5 mm.	146°/18 mm. (Hanriot)	$d_4^{20}$ 1.3416 $d_4^{20}$ 1.3241	$d_4^{20}$ 1.328 (Hanriot)
$\beta$ -Dichloro-hydrin	81—81.5°/ 13.5 mm.	182°/1 atm. (Tollens)	$d_4^{20}$ 1.3745 $d_4^{20}$ 1.3534	$d_4^{20}$ 1.3799 (Tollens)
$\beta$ -Monobromo-hydrin	136—138°/ 21 mm.	138°/17 mm. (Fink)	$d_4^{20}$ 1.7858	—
$\beta$ -Dibromo-hydrin	111—114°/ 20 mm.	115—120°/18 mm. (Kohler) 100°/10 mm. (Forster and Withers)	$d_4^{20}$ 2.1197	$d_4^{25}$ 2.1259 (Philip) $d_4^{20}$ 2.148 (Pariselle *)

\* *Ann. Chim.*, 1911, [viii], **24**, 387.

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