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# Rearrangement of Allylic Bromine accompanying the Addition of Hypobromous Acid to Allyl Bromide

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Hypobromous acid reacts with allyl bromide in water in the presence of perchloric acid to give 2,3-dibromopropan-1-ol (79%) and 1.3-dibromopropan-2-ol (21%). An isotope dilution experiment indicated that no other product was formed in significant amount. When the reaction was carried out with allyl [82Br] bromide, the resulting 2.3-dibromopropanol contained  $29 \pm 1\%$  of its radioactivity in the 2-position. When the bromine labelling was reversed, i.e., [82Br]hypobromous acid was added to inactive allyl bromide, the 3-position was labelled to the extent of  $30 \pm 1\%$ . This value, which is taken as a measure of the allylic bromine rearrangement, was reduced to 25% when the reaction was carried out in 40% dioxan-water. These results, together with earlier work on the corresponding chloro- and chlorobromo-systems, are discussed in terms of participation by neighbouring halogen groups in the intermediate carbonium ions.

CARBONIUM ions can, in suitable systems, undergo structural rearrangements; a group X attached to a particular carbon atom in the reactant may be attached to another carbon atom in the product. Even when X does not rearrange, it may cause a rate acceleration for a reaction by neighbouring-group participation, e.g., the rate of acetolysis of *trans*-2-bromocyclohexyl p-bromobenzenesulphonate<sup>1</sup> is faster than expected, as estimated from a comparison with the rate for the *cis* isomer and also from  $\sigma^* \rho^*$  correlations for other cyclohexyl p-bromobenzenesulphonates.<sup>2</sup>

Carbonium ions produced by electrophilic addition to olefins can also undergo rearrangement. In the hydration of allyl bromide,3 2-bromopropan-1-ol is formed (10%) together with the expected 1-bromopropan-2-ol. de la Mare and Pritchard<sup>4</sup> showed that the products of the reaction of hypochlorous acid with allyl [<sup>36</sup>Cl]chloride (X = Y = Cl in Scheme 1) contained 4% of the radioactivity in the 2 position of 2,3-dichloropropan-1-ol. When the electrophilic reagent was hypobromous acid <sup>5</sup> (X = Cl, Y = Br) the rearranged 3-bromo-2-chloropropan-1-ol formed less than 0.8% of the total product, whereas the effect of changing X first to bromine<sup>5</sup> then to iodine <sup>6</sup> caused the rearranged 2-X product to increase to 28 and 48%, respectively. These results

<sup>1</sup> S. Winstein, E. Grunwald, and L. L. Ingraham, J. Amer. Chem. Soc., 1948, 70, 821.

 <sup>a</sup> A. Streitweiser, jun., Chem. Rev., 1956, 56, 694.
 <sup>a</sup> C. A. Stewart and C. A. Van der Werf, J. Amer. Chem. Soc., 1954. 76 1259.

accord with Scheme 1. The electrophilic reagent attaches Y to the particular carbon atom which is known to be attacked by other electrophiles (e.g.,  $H^+$ ) forming carbonium ion (I) which can partition itself



between the isomeric non-rearranged products by nucleophilic attack of a water molecule at carbon atom 1 or 2. The rearranged product must arise from an intermediate such as (II) where there is some interaction between the group X and the carbonium ionic centre. The increase in the rearranged product  $4 \rightarrow 28$ 

P. B. D. de la Mare and J. G. Pritchard, J. Chem. Soc., 1954,

<sup>3910.</sup> <sup>5</sup> P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, J. Chem. Soc., 1962, 443. • P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams,

J. Chem. Soc., 1963, 3429.

 $\longrightarrow$  48% as X changes from Cl  $\longrightarrow$  Br  $\longrightarrow$  I is as expected for the increasing neighbouring-group participation of the halogens along the series, and also from the trend of the decreasing C-Halogen bond strengths Cl > Br > I.

Since it is of interest to examine the case of X = Y = Br, to determine which bromine atom here competes the more effectively for the positive centre, we have analysed the products (for the position and extent of radioactive labelling) of the reaction of (a) hypobromous acid with allyl [<sup>82</sup>Br]bromide and (b) [<sup>82</sup>Br]-hypobromous acid with inactive allyl bromide.

# EXPERIMENTAL AND RESULTS

Quantitative kinetic analyses of the dibromopropanol mixtures were carried out (cf. ref. 4) by following the reaction of sodium hydroxide with the dibromopropanol mixture (both ca. 0.05M) in water at  $0^{\circ}$ .

Radioactivity was measured on a well-type scintillation counter. Samples were weighed directly into the cells used for counting and were made up to 5 ml. with

sodium sulphate and extracted with ether, the ether solution dried, and the ether removed. The residue was fractionated, mixed dibromopropanols (11.4 g.) being collected at 64-65°/0·1 mm. (yield 56% on hypobromous acid used) (Found: C, 16.5; H, 2.75; Br, 73.3. Calc. for  $C_{3}H_{6}OBr_{2}$ : C, 16.5; H, 2.75; Br, 73.4%). A sample of the mixed dibromopropanols was kept for kinetic analysis and for radioactivity measurement. The remainder (ca. 11 g.) was allowed to react with 1n-sodium hydroxide (15% excess over 1,3-dibromopropan-2-ol present) for 30 min. at room temperature. The mixture was extracted with ether. The extract, after removal of ether and epibromohydrin, was fractionated and the dibromopropanol (5.5 g.) collected 64-65°/0.1 mm. Kinetic analysis of the product indicated 98% 2,3-dibromopropan-1-ol. A sample was kept for counting and the remainder allowed to react to completion with 10% excess of aqueous sodium hydroxide. The solution was extracted with ether and after removal of ether, epibromohydrin (1 g.) was collected at 130-132°/760 mm. (Found: C, 26.0; H, 3.6; Br, 59.0. Calc. for C<sub>3</sub>H<sub>5</sub>OBr: C, 26.3; H, 3.65; Br, 58.4%).

Method II. This method was used when there was insufficient material or level of radioactivity to complete



ethanol. The results were corrected for background and dead-time. Radio activity is expressed as specific activity in counts min.<sup>-1</sup> mmole<sup>-1</sup>. All counts relating to a particular reaction were done consecutively on the same counter, thus eliminating the need for corrections due to the decay of the activity. Radioactive bromine was supplied as unprocessed NH<sub>4</sub> <sup>83</sup>Br by A.E.R.E. Harwell.

Commerical allyl bromide was washed with ferrous sulphate solution, then with water, dried, and fractionated. It had b. p.  $70.0-70.5^{\circ}/760$  mm.

Allyl [82Br]Bromide.—NH<sub>4</sub> 82Br (ca. 5 mc, ca. 0.1 g.) and inactive lithium bromide (ca. 1 g.) were dissolved in a small volume of water and the water removed. The residue was extracted with dry acetone, allyl bromide (ca. 30 ml.) added, and the whole refluxed for 12 hr. When cold the mixture was washed with ice-cold water, the organic layer separated, dried, and fractionated. Labelled allyl bromide was collected at  $70.0-70.5^{\circ}/760$  mm.

Hypobromous acid was prepared in the usual way <sup>7</sup> by shaking a bromine solution with silver phosphate for 2 hr. The mixture was distilled under reduced pressure at 25—30°, the hypobromous acid solution (*ca.* 0.15M) being collected in ice. [<sup>82</sup>Br]Hypobromous acid was prepared in the same way with a little  $\rm NH_4$  <sup>82</sup>Br added to the bromine solution before it was shaken with silver phosphate.

The products were analysed by one of two methods.

Method I. Hypobromous acid (0.093 mole) was added to a saturated solution of allyl bromide in water (ca. 3.5 l.) containing perchloric acid (0.02M). Reaction was complete almost instantaneously. The mixture was saturated with

analysis by Method I. The reaction was carried out as described for Method I and the mixed dibromopropanols isolated. A sample was kept for radioactive counting and the rest converted completely into epibromohydrin by reaction with aqueous alkali. The epibromohydrin was isolated, purified, and counted. This shorter method assumes that 1,3-dibromopropan-2-ol (21% of total; see kinetic analysis results) labelled with <sup>82</sup>Br gives on treatment with alkali 10.5% labelled and 10.5% inactive epibromohydrin (Scheme 2). Consistent results were obtained by both methods for reaction of (a) labelled allyl bromide with unlabelled HOBr and (b) unlabelled allyl bromide with labelled HO<sup>82</sup>Br, although there was evidence of some bromine exchange within the dibromopropanols when they were subjected to high temperatures for a longer time. In view of this consistency, exchange of bromine atoms is not thought to be appreciable in distillations at lower temperatures.

Kinetic Analyses.—(a) Mixed dibromopropanols isolated from the reaction mixture. Both the dibromopropanols and sodium hydroxide were 0.0482M in water. The reaction was carried out at 0°. Samples (10 ml.) were withdrawn at intervals, run into standard acid, and back-titrated with standard alkali. Plots of 1/(a - x) against time were drawn. The rate constant  $k_2$ , calculated from the slope of the line, was 0.40 l. mole<sup>-1</sup> min.<sup>-1</sup>, whilst from the intercept the proportion of the more slowly reacting 2,3-dibromopropan-1-ol was 79% (Table 1). Duplicate runs gave 0.39, 0.42, and 78, 79%.

<sup>7</sup> P. B. D. de la Mare and J. T. Harvey, J. Chem. Soc., 1956, 36.

			Table	1			
t (min.) Titre (ml.)	0 0·52	1·8 2·79	4·5 3·10	6∙9 3∙38	11∙6 3∙80	$17.5 \\ 4.32$	$24 \cdot 1 \\ 4 \cdot 76$
t (min.) Titre (ml.)	29·7 5·04	35.9 5.38	${}^{42\cdot 6}_{5\cdot 72}$	$47.3 \\ 5.88$	∞ 10·38	$ \begin{array}{c} \infty & (a) \\ 3 & 10^{-1} \end{array} $	calc.) 52
			Table	2			
t (min.) Titre (ml.)	0 0·52	2	2·5 1·08	$5.6 \\ 1.68$	9·7 2·2	7 28	$15.8 \\ 3.04$
t (min.) Titre (ml.)	$25.7 \\ 3.98$	<b>3</b> 8	3·5 1·90	$49.5 \\ 5.52$	∞ 10-4	۰ م	) (calc.) 10·52

(b) Dibromopropanols recovered after treatment with alkali (Table 2). From a graph, 2,3-dibromopropan-1-ol = 98%,  $k_2 = 0.41$  l. mole<sup>-1</sup> min.<sup>-1</sup>. A commercial sample of 2,3-dibromopropan-1-ol gave a purity of 89% and  $k_2 0.48$  l. mole<sup>-1</sup> min.<sup>-1</sup>.

(c) Change of solvent. The products from the reaction carried out in both 40 and 70% dioxan-water gave the percentage of 2,3-dibromopropan-1-ol as 79%.

Results of Radioactivity Counting.-These are shown in Tables 3 and 4. Some reactions with labelled allyl bromide

### TABLE 3

Method I		
Weight taken	Corrected counts/min.	Specific activity
0·1833 g.	19,801 $\pm$ 140	$23,560 \pm 170$
$0.0893 \\ 0.0782$	$\begin{array}{r} 9741 \pm 70 \\ 4011 \pm 35 \end{array}$	${\begin{array}{r} 23,760 \pm 120 \\ 7020 \pm 60 \end{array}}$
	Method I Weight taken 0.1833 g. 0.0893 0.0782	$\begin{array}{ll} \mbox{Method I.} & & \\ \mbox{Weight} & & \mbox{Corrected} \\ \mbox{counts/min.} & \\ \mbox{0.1833 g.} & \mbox{19,801} \pm \mbox{140} \\ \mbox{0.0893} & \mbox{9741} \pm \mbox{70} \\ \mbox{0.0782} & \mbox{4011} \pm \mbox{35} \\ \end{array}$

Proportion of [3-82Br] 2,3-dibromopropan-1-ol, labelled in 3 position =  $7020/23,760 = 29.5 \pm 1\%$ .

Rearrangement product as a percentage of the total product =  $29.5 \times \frac{79}{100} = 23 \pm 1\%$ .

### TABLE 4

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From	labelled	allvl	bromide.	Method II.

Sample	Weight taken	Corrected counts/min.	Specific activity
Allyl bromide	0·4175 g.	$9026 \pm 95$	$2613 \pm 28$
Mixed dibromopropanols	0·8810	$10,864 \pm 105$	$2657 \pm 21$
Epibromohydrin	0.7821	$9811 \pm 100$	$1717 \pm 18$
<b>n</b>			

Rearrangement product as a percentage of the total product =  $24.5 \pm 1\%$ . Duplicate values of 21.5, 21.0, and 24.5%were also obtained.

(Table 4) were carried out in the presence of silver ion (0.002M). This did not seem to affect the result. The mean value of the percentage of rearrangement product is taken as  $23 \pm 1\%$ . The reaction was also carried out in 40% dioxan solvent using labelled HO<sup>82</sup>Br, the products being analysed by Method II. The percentage of rearrangement product was  $20 \pm 1\%$ .

Isotope Dilution.-Hypobromous acid (0.0317 mole) was added to a saturated solution of labelled allyl bromide (specific activity  $S_1 = 792 \pm 12$ ) in water (total volume 2010 ml.) containing perchloric acid (0.02m) and silver perchlorate (0.002M). When reaction was complete a sample of inactive mixed dibromopropanols (3.4554 g.) was added to 500 ml. of the reaction mixture and the whole shaken to make homogeneous. A sample of mixed dibromopropanols was extracted in the usual way. Its

<sup>8</sup> P. Ballinger, P. B. D. de la Mare, and D. L. H. Williams, J. Chem. Soc., 1960, 2467. <sup>9</sup> L. Smith and S. Skyle, Acta Chem. Scand., 1950, **4**, 39.

specific activity  $S_2$  was 267  $\pm$  3. If W g. of dibromopropanol is produced in a 500 ml. portion of reaction mixture, then  $WS_1 = (W + 3.4554) S_2$ , from which  $W = 1.757 \pm 0.02$ g. The weight produced in the total volume =  $1.757 \times$  $2010/500 = 7.06 \pm 0.08$  g., this corresponds to a yield (based on the hypobromous acid used up) of dibromopropanols of  $102 \pm 3\%$ .

### DISCUSSION

The isotope dilution experiment shows that the two isomeric dibromopropanols account for  $102 \pm 3\%$  of the total products of the reaction of hypobromous acid with allyl bromide. No olefin (formed by proton-loss from carbonium-ion intermediates) seems to be produced, as was the case for addition of hypohalous acids to allyl chloride,<sup>4,5</sup> although these products constitute ca. 20% of the total in addition reactions to 2-substituted allyl compounds (e.g., ref. 8). By kinetic analysis of the dibromopropanol mixture, the ratio 79:21 was obtained for the isomer ratio 2,3-dibromopropan-1-ol:1,3-dibromopropan-2-ol. This agrees very well with the ratio of 4:1 reported by Smith and Skyle<sup>9</sup> for this reaction.

The radioactivity experiments indicated that  $29.5 \pm$ 1% of the 2,3-dibromopropan-1-ol (or 23% of the total product) contained bromine in the 2-position which was originally in the 3-position in the allyl bromide. It is thought that this rearrangement takes place in an intermediate carbonium ion via some kind of threemembered ring system.

The "normal" addition of hydrogen halides to allyl bromide results in the formation of the 1,2-dihalides in each case,<sup>10</sup> *i.e.*, electrophilic attack takes place at the terminal carbon atom in the olefin. The -CH<sub>2</sub>Br group is clearly ortho-para directing in electrophilic aromatic substitutions; <sup>11</sup> nitration of benzyl bromide giving only 5% of meta product. Both these results show that even though the -CH2Br group is possibly overall electron-attracting, hyperconjugative electron release is strong enough to control the orientation of products of electrophilic attack. It seems likely, by analogy, that the Br<sup>+</sup> part of hypobromous acid also becomes attached to the terminal carbon atom in allyl bromide, and at the same time sets up a partial attachment with the developing positive charge in C(2).

The path of the reaction of hypobromous acid with allyl [82Br]bromide can be expressed in terms of Scheme 1, with  $X = {}^{82}Br$  and Y = Br. The non-rearranged product [2,3-82Br]dibromopropan-1-ol (56%) is formed by nucleophilic attack of a water molecule on C(1) of intermediate (I) together with full attachment of Br to C(2), whilst the rearranged product [2-82Br]3-dibromopropan-1-ol (23%) must be produced from the other intermediate carbonium ion (II) where the <sup>82</sup>Br atom is also interacting with the carbonium ionic centre, in competition with the entering bromine. The remaining product 1,3-dibromopropan-2-ol (21%) can arise by attack of a water molecule at C(2) in both intermediates.

<sup>10</sup> M. S. Kharasch and C. Hannum, J. Amer. Chem. Soc., 1934, **56**, 1782; M. S. Kharasch and F. R. Mayo, *ibid.*, 1933, **55**, 2461. <sup>11</sup> B. Flürscheim and E. L. Holmes, J. Chem. Soc., 1928, 1607. It has been suggested  $^{12,13}$  that many reactions of halogens with olefins proceed at least in part *via* the fully formed three-membered cyclic halonium ion. We prefer to consider that this type of intermediate (VI) contributes to the final structure of (I) which is regarded

$$\begin{array}{ccc} CH_2 - CH CH_2^{82}Br & CH_2 - \overset{-}{C}H CH_2^{82}Br & \overset{+}{C}H_2 CHBr CH_2^{82}Br \\ & & \\ Br & & \\$$

as a resonance hybrid of (VI), (VII), (VIII), and possibly other species. It is probable that structure (VI) makes a bigger contribution in the present reaction than the equivalent chloronium ions do in additions of hypochlorous acid <sup>4</sup> because of the increasing tendency Cl < Br for the halogen to increase its covalency.

This work is concerned mainly with the extent of the rearrangement product, 23% of the total. From comparisons of this figure with earlier results, the following points emerge.

(a) With allylic chlorine (Y = Cl) there is very little rearrangement irrespective of whether the entering halogen is chlorine <sup>4</sup> (4%) or bromine <sup>5</sup> (<0.8%). This is in agreement with the low value of the driving force estimated <sup>14</sup> for neighbouring-group participation by chlorine. The small difference lies in the expected direction, *i.e.*, Y competes more effectively with entering chlorine than with bromine.

(b) When the allylic halogen is bromine (X = Br), the extent of rearrangement is, as expected, greater than for chlorine (X = Cl), the values being 28% for entering chlorine <sup>5</sup> (Y = Cl) and 23% for entering bromine. Again the extent of the rearrangement is not very dependent on Y, with the small difference being in the same direction as before.

The effect of change of Y from Cl to Br is shown more clearly in Table 5, where reactions are virtually free from complications due to rearrangements.

### TABLE 5

2-Y isomer (%) in the products of addition of HOY to

	(a)	(b)	(C)
HOY	CH2=CH•CH3	CH <sub>2</sub> =CH·CH <sub>2</sub> OH·	CH2=CH·CH2CI
HOCI	9 8	27 °	70 4
HOBr	21 12 *	34 9	74 5
ноі			716

## \* Electrophilic reagent BrCl.

For (b) and (c) there is only a relatively small change in the proportion of 2-Y isomer as Y is changed from Cl to Br and to I. The value is greater for Y = Br than for Y = Cl, as expected from considerations of the extents of neighbouring-group participation by Y (although the value for I seems slightly anomalous). The change is greater in case (a) although here Br-Cl was one of the electrophilic reagents and possibly the two results are not strictly comparable. These results indicate that at least where the 2-Y isomer is produced to an appreciable

 $^{12}$  P. B. D. de la Mare and S. Galandauer, J. Chem. Soc., 1958, 36.

extent, a change of Y from Cl to Br does not increase this figure by very much, *i.e.*, this change of electrophile has only a secondary effect. This suggests that the partitioning of the intermediate among the 1-Y and 2-Y products depends very largely on the polar requirements of the system and only to a small extent upon neighbouring-group participation by Y. The attachment of Y to C(1) and C(2) probably takes place simultaneously, since the partition between 1-Y and 2-Y products is not markedly dependent on solvent composition.<sup>5</sup>

Results for the rearrangement of X are summarised in Table 6. As expected, the percentage rearranged 2-X isomer increases across Table 6, but varies little for any

TABLE	6
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% 2-X isomer in the products of addition of HOY to

		CH2=CH•CH2X	
HOY	X = Cl	$\mathbf{X} = \mathbf{Br}$	X = I
носі	4 4	28 5	48 <sup>6</sup>
HOBr	<0.8 2	23	
НОІ	ca. 0 <sup>8</sup>		

one X as Y is changed. It appears that the amount of rearrangement in this system is governed almost entirely by the neighbouring-group participation of X which increases Cl < Br < I, and by the strength of the C-X bond which decreases Cl > Br > I, and is only very slightly dependent on the strength of the competition from the entering halogen Y. So X competes with entering bromine only very slightly less effectively than it does with entering chlorine. The distribution of isomeric products (III): (IV): (V) from the reaction of hypobromous acid with allyl bromide (56:21:23) is much more like that from hypochlorous acid with allyl bromide (40:32:28) than that from hypochlorous acid with allyl chloride (66:30:4).

Variation of Solvent.---The decrease in the extent of rearranged products in these systems in less polar solvents (dioxan-water) has been attributed 5,6 to decreased stabilities of the carbonium ions which have a shorter life in which to undergo structural rearrangement. In the reaction of hypobromous acid and allyl bromide one determination in 40% dioxan-water indicated 20%rearrangement compared with 23% in pure water. This difference is barely significant. Also, kinetic analysis of products isolated from the reaction in 40 and also 70% dioxan-water gave consistent values of 79% for the percentage of 2,3-dibromopropan-1-ol. It is possible that the intermediate carbonium ion (I) is more stable when Y = Br than when Y = Cl, because of a greater contribution by structure (VI), and so the lifetime of the intermediate is not so dependent on the solvent composition.

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68, 536; 1948, 70, 828, 841, 846.

E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, 1959, p. 523.
 S. Winstein and E. Grunwald, J. Amer. Chem. Soc., 1946.