

**636.** *The Kinetics and Mechanisms of Additions to Olefinic Substances. Part IX.<sup>1</sup> Rearrangement Accompanying Addition of Hypochlorous Acid to Allyl Iodide, and Related Reactions.*

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The addition of hypochlorous acid to allyl iodide in aqueous perchloric acid gives 1-chloro-3-iodopropan-2-ol, 2-chloro-3-iodopropan-1-ol, and 3-chloro-2-iodopropan-1-ol in the ratio 30 : 22 : 48. The amount of the last product, of migration of iodine from the 3- to the 2-position, is reduced to 30% and 18%, respectively, when the addition is carried out in mixtures of dioxan and water containing 40% and 70% of dioxan. The addition of iodine chloride to allyl alcohol gives 2-chloro-3-iodo- (30%) and 3-chloro-2-iodopropan-1-ol (70%); no 1-chloro-3-iodopropan-2-ol, the product of hydroxyl-migration, was detected. Similarly, the addition of the elements of hypoiodous acid to allyl chloride gives 1-chloro-3-iodopropan-2-ol (29%) and 3-chloro-2-iodopropan-1-ol (71%), with no detectable product, 2-chloro-3-iodopropan-1-ol, of chlorine-migration. The significance of these results is discussed in terms of the nature of the intermediates concerned in these addition reactions.

In previous papers in this series, the additions of hypochlorous acid to allyl chloride<sup>2</sup> and to allyl bromide<sup>1</sup> have been described. The amount of product from migration of the allylic halogen from the 3- to the 2-position during the addition was 4% for allyl chloride and 28% for allyl bromide. This migration was considered to result from neighbouring-group interaction of the allylic halogen with the carbonium ionic centre in an intermediate; the larger amount of migration of allylic bromine than of allylic chlorine was attributed to the greater neighbouring-group participation<sup>3</sup> of bromine and the easier heterolysis of the C-Br bond.

On this basis it might be expected that the amount of allylic migration would be even greater for allylic iodine, provided that the life-times of the intermediates concerned in this case were similar to those for the additions to allyl chloride and allyl bromide, because iodine<sup>3</sup> has a greater neighbouring-group participation than bromine and the C-I bond is easily heterolysed. Consequently we have examined the addition of hypochlorous acid to allyl iodide under conditions similar to those employed for the same addition to allyl chloride and allyl bromide.

Although 1-chloro-3-iodopropan-2-ol is a well-characterised compound obtained<sup>4</sup> by ring-opening of epichlorohydrin or of epi-iodohydrin, the isomeric 2-chloro-3-iodo- and 3-chloro-2-iodopropan-1-ol had previously been described only as mixtures<sup>5,6</sup> derived by addition of iodine chloride to allyl alcohol. We have prepared the pure isomers through sequences analogous to those used for the corresponding bromochloropropanols.<sup>1</sup> 2-Chloro-3-iodopropan-1-ol was obtained by adding iodine chloride to allyl alcohol and then destroying the more reactive isomer, 3-chloro-2-iodopropan-1-ol, by reaction with alkali. 3-Chloro-2-iodopropan-1-ol was prepared by adding hypoiodous acid to allyl chloride and destroying with alkali the more rapidly reacting 1-chloro-3-iodopropan-2-ol also present in the reaction mixture. The purity of each isomer was confirmed from its infrared spectrum and by kinetic analysis with alkali. Vapour-phase chromatography under the conditions used by us separated 1-chloro-3-iodopropan-2-ol from the primary

<sup>1</sup> Part VIII, de la Mare, Naylor, and Williams, *J.*, 1962, 443.

<sup>2</sup> de la Mare and Pritchard, *J.*, 1954, 3910.

<sup>3</sup> Winstein and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

<sup>4</sup> Reboul, *Annalen*, 1861, *Suppl.* 1, 218; Blanchard, *Bull. Soc. chim. France*, 1927, **41**, 824; Kling, *Compt. rend.*, 1903, **137**, 756.

<sup>5</sup> Bigot, *Ann. Chim. Phys.*, 1891, [6], **22**, 433; Nilsson and Smith, *Svensk kem. Tidskr.*, 1944, **56**, 156; Garreau, *Compt. rend.*, 1950, **230**, 448.

<sup>6</sup> Noland and Bastian, *J. Amer. Chem. Soc.*, 1955, **77**, 3395.

isomers, but did not separate 2-chloro-3-iodopropan-1-ol from 3-chloro-2-iodopropan-1-ol; similar behaviour had been observed<sup>1</sup> for the corresponding bromochlorohydrins.

#### EXPERIMENTAL

The purification of allyl chloride, allyl alcohol, and dioxan, the preparation of hypochlorous acid, and the experimental procedure for kinetic analysis of halogenohydrins with alkali, have been described elsewhere.<sup>2,7,8</sup> Iodine chloride, purified by redistillation of the commercial product, had b. p. 97.4°. Allyl iodide was purified by shaking the deep red commercial product with dilute aqueous sodium thiosulphate to remove free iodine. The product was washed with water, dried (CaSO<sub>4</sub>), and fractionally distilled with the exclusion of light as far as possible, b. p. 103°/760 mm. Although stored in a dark bottle and generally used as soon as possible after distillation, the allyl iodide used was tinted slightly red.

Infrared spectra of thin films of liquid between rock-salt plates were recorded on a Grubb-Parsons DB2 double-beam grating spectrophotometer.

Gas chromatograms were recorded on a Griffin and George instrument. A column (12' × ¼") packed with Silicone oil on Celite was used at 155° (N<sub>2</sub> flow-rate 1.9 l. per hr.). Quantitative analysis involved comparison of peak-areas as in our earlier work.<sup>1</sup>

**1-Chloro-3-iodopropan-2-ol.**—Concentrated hydriodic acid (100 ml.) was added dropwise with stirring to a slight excess of epichlorohydrin (60 ml.). The neutral aqueous layer was separated off, the organic layer dried (Na<sub>2</sub>SO<sub>4</sub>), and excess of epichlorohydrin removed *in vacuo* at 50°. The remainder was fractionated and gave 1-chloro-3-iodopropan-2-ol (130 g., 80%), b. p. 89—91°/1.5 mm. (Found: C, 16.5; H, 2.8; Hal, 73.8. Calc. for C<sub>3</sub>H<sub>6</sub>ClIO: C, 16.3; H, 2.7; Hal, 73.7%). In its reaction with alkali at 25° the theoretical infinity (calculated on the basis of conversion into epichlorohydrin) was reached within 5 min. Analysis by vapour-phase chromatography established the absence of both the isomeric primary alcohols.

**2-Chloro-3-iodopropan-1-ol.**—Iodine chloride (80 g.) was dissolved in *n*-hydrochloric acid (3 l.). Allyl alcohol (*ca.* 30 g.) was added dropwise, the reaction mixture being shaken in the dark until the colour of the iodine chloride had disappeared. The chloriodopropanols were salted out (with Na<sub>2</sub>SO<sub>4</sub>, 1 kg.) and extracted into ether (3 × 300 ml.). The ether extracts from four such reactions were combined and dried (Na<sub>2</sub>SO<sub>4</sub>). The ether was removed *in vacuo* and the chloriodopropanols were fractionally distilled (312 g., 75%; b. p. 90—91°/1.5 mm.). This mixture was shown by kinetic analysis to contain about 30% of 2-chloro-3-iodopropan-1-ol. A portion (250 g.) was treated with 80% of its equivalent of aqueous 0.065*N*-sodium hydroxide (15 l.). After completion of the reaction, the remaining chloriodopropanols were recovered as before; fractionation gave a mixture of chloriodopropanols (49 g.), b. p. 91°/1.5 mm., which was found by kinetic analysis to contain 85% of 2-chloro-3-iodopropan-1-ol. The 2-chloro-3-iodo-isomer was further enriched by treating this mixture (48 g.) with its equivalent of 0.044*N*-sodium hydroxide (5 l.) for 20 min. at 25°. On recovery as before there was obtained 2-chloro-3-iodopropanol (20 g.), b. p. 91—92°/1.5 mm. (Found: C, 16.5; H, 2.8; Hal, 73.9%).

For kinetic analysis, 2-chloro-3-iodopropan-1-ol (1.27 g.) was added to an equivalent amount of aqueous sodium hydroxide (150 ml.; 0.0384*N*) at 25°. Samples (10 ml.) were withdrawn at intervals, added to a known excess of 0.0500*N*-acid, and back-titrated with 0.0500*N*-sodium hydroxide. The results are given in the Table.

Time (min.)	0.0	2.7	8.9	16.8	24.8	35.0	46.2	55.5	66.0	80.0	$\infty_{\text{obs}}$	$\infty_{\text{calc}}$
Titre (ml. 0.0500 <i>N</i> -NaOH)	2.35	2.68	3.37	4.10	4.72	5.31	5.79	6.16	6.47	6.82	9.98	10.00
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	—	0.443	0.451	0.463	0.473	0.471	0.463	0.467	0.463	0.460	—	—

From the graph of  $1/(A - x)$  against  $t$  (where  $A$  is the initial concentration of alkali and  $x$  is the amount used up after time  $t$ ) the purity of the 2-chloro-3-iodopropanol is 100% and its rate coefficient ( $k_2$ ) for alkaline hydrolysis at 25° is 0.46 l. mole<sup>-1</sup> min.<sup>-1</sup>.

**3-Chloro-2-iodopropan-1-ol.**—Iodine chloride (80 g.) was dissolved in aqueous hydrochloric acid (4 l.; 0.2*N*). Allyl chloride (*ca.* 40 g.) was added dropwise, the mixture being shaken until all the iodine chloride was used up. The dichloriodopropanes settled to the bottom and

<sup>7</sup> de la Mare and Pritchard, *J.*, 1954, 3990.

<sup>8</sup> de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

were extracted with pentane. The remaining chloriodopropanols were salted out (1.2 kg. of  $\text{Na}_2\text{SO}_4$ ) and extracted with ether ( $4 \times 300$  ml.), the extract, dried ( $\text{Na}_2\text{SO}_4$ ), and the ether was removed under a vacuum. Fractional distillation gave chloriodopropanols (25 g.), b. p. 89—92°/1.5 mm. This mixture was shown by kinetic analysis to contain *ca.* 70% of the 3-chloro-2-iodo-isomer. It was treated with 40% of its equivalent of 0.029N-sodium hydroxide (1.5 l. for 23.8 g.). On completion of the reaction, recovery as before gave 3-chloro-2-iodopropan-1-ol (10 g.), b. p. 90—92°/1.5 mm. (Found: C, 16.5; H, 2.8; Hal, 72.0%).

Vapour-phase chromatography gave only one peak, but kinetic analysis revealed the presence of a little of the more reactive isomer. 3-Chloro-2-iodopropan-1-ol (1.148 g.) was added to an equivalent amount of aqueous sodium hydroxide (150 ml.; 0.0347N) at 0°. Samples (10 ml.) were withdrawn at intervals and added to 0.0500N-hydrochloric acid (10 ml.), and the excess of acid was back-titrated with 0.0347N-sodium hydroxide.

From the graph of  $1/(A - x)$  against  $t$ , the purity of the 3-chloro-2-iodopropan-1-ol is 97% and its rate coefficient ( $k_2$ ) for alkaline hydrolysis at 0° is 0.29 l. mole<sup>-1</sup> min.<sup>-1</sup>. Further purification

Time (min.)	0.0	4.8	10.2	20.0	30.5	40.0	50.2	60.0	72.0	83.5	100.0	$\infty_{\text{obs}}$
Titre (ml. 0.0347N-NaOH)	4.45	5.10	5.54	6.24	6.89	7.41	7.84	8.25	8.66	9.00	9.47	14.34
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	—	0.432	0.348	0.317	0.308	0.306	0.298	0.297	0.294	0.292	0.294	—

was not attempted, since with such a reactive compound it would have involved prohibitive loss of material. Treatment with alkali gave epichlorohydrin, identified by its b. p. and vapour-phase chromatography.

The infrared spectra of the isomeric chloriodopropanols are recorded in Table I.

TABLE I.

Infrared spectra (cm.<sup>-1</sup>; 545—1460 region) of isomeric chloriodopropanols.

1-Chloro-3-iodopropan-2-ol				2-Chloro-3-iodopropan-1-ol				3-Chloro-2-iodopropan-1-ol				
884w	1080m			575s	853m	1104m		565m	877vw	1089m	1285w	
629m	905w	1124m	1342w	606m	885m	1134m	1330w	606m	894w	1125m	1314w	
705m	924vw	1176m	1379w	660m	910vw	1176s	1393m	705s	910w	1175m	1330w	
	959vw	1202m		724m	1205m	1425m	963s		963m	1205w	1374m	
758s	974w		1427s	741m	1242w	1431m		745vw		1227w	1393w	
806m	1033s	1253m		757m	1253m	1460m	1033m		1007m	1242w	1431m	
852m	1064m	1295m		839m	1299vw		1050s	846w	1050s	1274m	1456m	

*Products of Addition of Iodine Chloride to Allyl Alcohol.*—The reaction was carried out as described for the preparation of 2-chloro-3-iodopropanol, though on a smaller scale, by using iodine chloride (80 g.) in 0.5N-hydrochloric acid (3 l.). The chloriodopropanols (67 g., 65%) had b. p. 89—91°/1.5 mm. The infrared spectra of the products showed the presence of 2-chloro-3-iodopropan-1-ol and 3-chloro-2-iodopropan-1-ol. Vapour-phase chromatography gave only one peak, thus confirming the absence of 1-chloro-3-iodopropan-2-ol. For kinetic analysis, the chloriodopropanol mixture (1.224 g.) was added to alkali (150 ml.; 0.0370N) at 25°. Samples (10 ml.) were withdrawn at intervals and added to 0.0500N-acid (10 ml.), and the excess of acid was back-titrated with 0.0370N-sodium hydroxide.

Time (min.)	0	23.2	30.3	39.0	49.5	60.0	70.2
Titre (ml. 0.0370N-NaOH)	3.54	10.72	10.86	10.99	11.14	11.24	11.31
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) *	—	—	—	—	0.651	0.567	0.503
Time (min.)	80.0	91.5	100.0	112.2	$\infty_{\text{obs}}$	$\infty_{\text{calc}}$	
Titre (ml. 0.0370N-NaOH)	11.47	11.50	11.57	11.64	13.37	13.50	
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) *	0.620	0.522	0.530	0.513	—	—	

\*  $t = 39$  min. as zero time.

From the graph of  $1/(A - x)$  against  $t$ , the amount of 2-chloro-3-iodopropanol is 31.0% and its rate coefficient ( $k_2$ ) is 0.52 l. mole<sup>-1</sup> min.<sup>-1</sup> at 25°. For the product from a second experiment in which addition was carried out in N-hydrochloric acid, the amount of 2-chloro-3-iodopropanol was found similarly to be 29.7%.

*Addition of Hypoiodous Acid to Allyl Chloride.*—This reaction was carried out as described for the preparation of 3-chloro-2-iodopropan-1-ol, iodine chloride (80 g.) being dissolved in aqueous hydrogen chloride (4 l.). The chloriodopropanols had b. p. 89—92°/1.5 mm., the

Time (min.) .....	0	5.6	10.8	20.7	29.9	40.0	50.2
Titre (ml. 0.0332N-NaOH) ...	5.08	8.08	8.38	8.75	9.10	9.39	9.66
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) * .....	—	—	—	—	0.306	0.280	0.274
Time (min.) .....	60.0	70.3	81.8	92.5	102.2	$\infty_{\text{obs}}$	$\infty_{\text{calc}}$
Titre (ml. 0.0332N-NaOH) ...	9.88	10.11	10.29	10.53	10.70	15.00	15.04
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) * .....	0.266	0.265	0.253	0.262	0.262	—	—

\*  $t = 20.7$  taken as zero.

yields being 10.7 g., 20 g., and 24.9 g. in N-, 0.5N-, and 0.2N-hydrochloric acid, respectively. The mixtures contained 1-chloro-3-iodopropan-2-ol and 3-chloro-2-iodopropan-1-ol, as judged by their infrared spectra; no 2-chloro-3-iodopropan-1-ol was detected.

Above are given details of kinetic analysis of the product from the addition in N-hydrogen chloride. The chloriodopropanol mixture (1.099 g.) was added to sodium hydroxide (150 ml.; 0.0332N) at 0°. Samples (10 ml.) were withdrawn at intervals and added to 0.0500N-hydrochloric acid (10 ml.); the excess of acid was back-titrated against 0.0332N-sodium hydroxide. From the graph, the mixture contains 70.8% of 3-chloro-2-iodopropan-1-ol, and  $k_2 = 0.26$  l. mole<sup>-1</sup> min.<sup>-1</sup> at 0°.

Vapour-phase chromatographic analysis of the same mixture gave 72.0% of (3-chloro-2-iodopropan-1-ol + 2-chloro-3-iodopropan-1-ol); these isomers are not separated by this technique under our conditions. The agreement with the kinetic analysis is within experimental error and confirms the conclusion (reached from the infrared spectra) that very little, if any, migration of the allylic chlorine from the 3- to the 2-position occurred in this reaction. Kinetic analysis of the product from reaction in 0.5N- and in 0.2N-hydrochloric acid gave 69.6% and 71.4%, respectively, of 3-chloro-2-iodopropan-1-ol; the mean value adopted in the discussion is 71%.

*Addition of Hypochlorous Acid to Allyl Iodide.*—The addition was carried out in (a) aqueous N-perchloric acid, (b) 40% dioxan containing 0.02N-perchloric acid, and (c) 70% dioxan containing 0.02N-perchloric acid.

(a) Hypochlorous acid (500 ml.; 0.215M) was added to an excess of allyl iodide in N-perchloric acid (4 l.). Allyl iodide is rather insoluble under these conditions, and so the mixture was shaken for several hours. The resulting chloriodopropanols (5 g., 21%), isolated in the usual way, had b. p. 89–93°/1.5 mm.

(b) From the reaction between hypochlorous acid (1 l.; 0.0257M) and allyl iodide (50 g.) in 40% dioxan containing 0.02N-perchloric acid, there were obtained chloriodopropanols (18 g., 32%), b. p. 89–92°/1.5 mm.

(c) From hypochlorous acid (750 ml.; 0.257M) and allyl iodide (36 g.) in 70% dioxan containing 0.02N-perchloric acid there were obtained chloriodopropanols (5 g., 12%), b. p. 89–94°/1.5 mm.

These mixtures were analysed kinetically. Thus the chloriodopropanol mixture (a) (1.218 g.) was added to sodium hydroxide (150 ml.; 0.0368N) at 25°. Samples (10 ml.) were

Time (min.) .....	0.0	10.0	20.2	27.0	36.2	45.1	55.3
Titre (ml. 0.0368N-NaOH) ...	3.61	11.27	11.47	11.55	11.59	11.69	11.74
$k_2$ (l. mol. <sup>-1</sup> min. <sup>-1</sup> ) * .....	—	—	—	—	0.30	0.55	0.49
Time (min.) .....	65.0	76.7	88.2	100.5	$\infty_{\text{obs}}$	$\infty_{\text{calc}}$	
Titre (ml. 0.0368N-NaOH) ...	11.80	11.85	11.91	11.96	13.34	13.57	
$k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) * .....	0.50	0.47	0.49	0.47	—	—	

\*  $t = 27.0$  taken as zero.

withdrawn at intervals, added to 0.0500N-hydrochloric acid (10 ml.), and the excess of acid was back-titrated with 0.0368N-sodium hydroxide. From the graph, the mixture contained 22.4% of 2-chloro-3-iodopropan-1-ol, and  $k_2 = 0.48$  l. mol.<sup>-1</sup> min.<sup>-1</sup> at 25°.

TABLE 2.

Products from addition of hypochlorous acid to allyl iodide.

Solvent	HClO <sub>4</sub> (N)	2-Chloro-3-iodopropanol 1-Chloro-3-iodopropan-2-ol		3-Chloro-2-iodopropan-1-ol
		(%, by kinetic analysis)	(%, by gas chromatography)	
Water .....	1.0	22	30	48
40% Dioxan	0.02	39	31	30
70% Dioxan	0.02	50	32	18

The proportion of 1-chloro-3-iodopropan-2-ol was determined by vapour-phase chromatography. The results are given in Table 2. The infrared spectra of the samples were consistent with the analytical results and confirmed the trends in the isomeric proportions.

#### DISCUSSION

Since the isomeric chloriodohydrins need to be prepared by methods which initially give mixtures and might involve rearrangements, it is necessary to consider the evidence for our structural assignments. This evidence is in a sense indirect, but we regard it as definitive. In part it is based on the analogies<sup>9, cf. 1,2,7</sup> that the primary dihalogenohydrins derived from glycerol are less reactive with alkali than are secondary halogenohydrins, and that iodine is more readily displaced than chlorine by nucleophiles;<sup>10</sup> it is supported by comparison of the vapour-phase chromatographic behaviour of the chloriodohydrins with that of corresponding bromochlorohydrins,<sup>1</sup> and by the fact that on the basis of our assignment we need to associate rearrangements only with situations where we would expect these to occur, and not to situations where these should not happen. (a) Only one isomer was obtained by treatment of epichlorohydrin with hydrogen iodide. This we regard as the expected 1-chloro-3-iodopropan-2-ol, as is confirmed by its very rapid reaction with alkali. (b) Two other isomers were obtained by treating allyl alcohol with iodine chloride. Both of these were less reactive than 1-chloro-3-iodopropan-2-ol with alkali. From one of them, epichlorohydrin could be obtained after treatment with alkali. This must be 3-chloro-2-iodopropan-1-ol. The other must be 2-chloro-3-iodopropan-1-ol, and this is confirmed by the fact that it is the least reactive with alkali.

*Addition of Iodine Chloride to Allyl Alcohol.*—The chloriodopropanols obtained from this addition consisted only of 2-chloro-3-iodopropan-1-ol (30%) and 3-chloro-2-iodopropan-1-ol (70%). The fact that no product of migration of the hydroxyl group (1-chloro-3-iodopropan-2-ol) is obtained is consistent with the difficulty of heterolysis of the C-OH bond, and in agreement with the results of other additions to allyl alcohol.<sup>1,11</sup> Noland and Bastian,<sup>6</sup> from a study of the product of reaction of such a chloriodopropanol mixture with alkali, had concluded that the major product of the addition of iodine chloride to allyl alcohol is 2-chloro-3-iodopropan-1-ol, and not, as we have found, 3-chloro-2-iodopropan-1-ol. Their yields of 2-chloroallyl alcohol (16–19%) and epichlorohydrin (12–18%) obtained on treatment with alkali were, however, low, and their conclusion seems unjustified.

They suggested also, to account for the presence of epichlorohydrin after reaction with alkali, that a considerable amount of the original 2-chloro-3-iodopropan-1-ol may undergo replacement of iodine by chlorine, by further reaction with iodine chloride (cf. ref. 12):  $RI + ICl \rightarrow RCl + I_2$ . We have, however, found no evidence for the presence of 2,3-dichloropropan-1-ol in the product isolated after addition of iodine chloride to allyl alcohol; it is almost certain that their chloriodohydrin was a mixture and that their epichlorohydrin was derived from 3-chloro-2-iodopropan-1-ol.

The high yields (*e.g.*, 75% in *N*-HCl) of chloriodopropanols suggest that chloride ion is a much more effective nucleophile than water in competition for the carbonium ionic intermediate, an observation which is supported by the fact that the addition of iodine chloride to allyl chloride under similar conditions gives about 85% of dichloriodopropanes. In the corresponding addition of bromine chloride to allyl chloride, only 25% of bromodichloropropanes was obtained. This difference may not be general, however, since Galandauer<sup>13</sup> obtained very poor yields of iodochlorides on addition of iodine chloride to propene in aqueous hydrochloric acid.

<sup>9</sup> Smith, *Z. phys. Chem. (Leipzig)*, 1918, **92**, 717.

<sup>10</sup> Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185.

<sup>11</sup> Winstein and Goodman, *J. Amer. Chem. Soc.*, 1954, **76**, 4368; de la Mare, Naylor, and Williams, *Chem. and Ind.*, 1959, 1020.

<sup>12</sup> Keefer and Andrews, *J. Amer. Chem. Soc.*, 1954, **76**, 253.

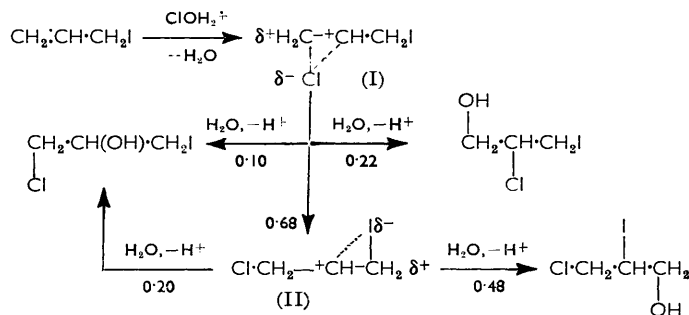
<sup>13</sup> Galandauer, M.Sc. Thesis, University of London, 1957; de la Mare and Galandauer, *J.*, 1958, 36.

*Addition of Hypoiodous Acid to Allyl Chloride.*—The addition gave only 3-chloro-2-iodopropan-1-ol (71%) and 1-chloro-3-iodopropan-2-ol (29%), an orientation similar to that which might have been expected by analogy with the corresponding additions of hypobromous acid<sup>1</sup> and hypochlorous acid<sup>2</sup> which gave, respectively, 73% of 2-bromo-3-chloropropan-1-ol and 70% of 2,3-dichloropropan-1-ol.

The fact that no 2-chloro-3-iodopropan-1-ol was detected, either by comparison of kinetic and vapour-phase chromatographic analysis or from the infrared spectrum of the product, confirms our view that in electrophilic halogen additions to allylic halides the migration of the allylic halogen is partly determined by its ability to compete effectively with the entering halogen for the carbonium ionic centre. Given sufficient time to become correctly orientated, an allylic chlorine competes on equal terms with the attacking chlorine, but it cannot compete effectively with the better participators, entering bromine or iodine. So in the additions of hypochlorous acid, hypobromous acid, and hypoiodous acid to allyl chloride, the amounts of migration of allylic halogen to the 2-position are, respectively, 4%, >0.7%, and small.

*Addition of Hypochlorous Acid to Allyl Iodide.*—In the addition of hypochlorous acid to allyl iodide the situation is quite different from that in the additions just discussed. Provided that the allylic iodine atom has time to become correctly orientated in the intermediate, it should compete very effectively with the attacking chlorine and with sufficient opportunity might gain complete control of the carbonium ionic centre. In fact, we find that the addition of hypochlorous acid to allyl iodide in aqueous perchloric acid gives 48% of 3-chloro-2-iodopropan-1-ol. Thus, for the addition of hypochlorous acid to allyl chloride,<sup>2</sup> allyl bromide,<sup>1</sup> and allyl iodide, migration of the allylic substituent from the 3- to the 2-position accounts, respectively, for 4%, 28%, and 48% of the product. The virtually complete control of the carbonium ion centre which would be predicted from the magnitude of neighbouring-group participation by iodine<sup>3</sup> is, however, not achieved, since some 2-chloro-3-iodopropan-1-ol is produced. This shows that the first-formed carbonium ion intermediate reacts rapidly, but not instantaneously, with other nucleophiles. Similar considerations apply to the addition of hypochlorous acid to allyl bromide,<sup>1</sup> where 40% of 2-chloro-3-bromopropan-1-ol is formed.

The amount of migration of the allylic iodine drops from 48% in water to 30% in 40% dioxan and 18% in 70% dioxan. It appears that in the less ionising dioxan-water mixtures the intermediate carbonium ion has a shorter life, so there is less time for the allylic iodine atom to gain control of the carbonium ion centre before the intermediate is destroyed by reaction with a nucleophile. A similar result was obtained for addition to allyl bromide.<sup>1</sup>



Analogy with the Scheme which we used to interpret the products of addition of hypochlorous acid to allyl bromide<sup>1</sup> leads to the attached Scheme for addition of hypochlorous acid to allyl iodide. We assume that 2-chloro-3-iodopropanol is formed only from the first intermediate (I), and that the intermediate (II) is partitioned as for the reaction of allyl chloride with hypoiodous acid, in which reaction it is the only intermediate concerned.

It follows that some of the 1-chloro-3-iodopropan-2-ol must be derived from the intermediate (I).

TABLE 3.  
Products of the addition of hypochlorous acid to allyl iodide.

Solvent	Proportion of 3-chloro-2-iodo- propan-1-ol observed	Proportion of 2-chloro-3-iodo- propan-1-ol		Proportion of 1-chloro-3-iodo- propan-2-ol			Obs.
		Calc.	Obs.	Calc. from (I)	Calc. from (II)	Calc. total	
Water; 1N-HClO <sub>4</sub> .....	0.48	—	0.22	—	—	—	0.30
40% Dioxan; 0.02N-HClO <sub>4</sub> ...	0.30	0.40	0.39	0.18	0.12	0.30	0.31
70% Dioxan; 0.02N-HClO <sub>4</sub> ...	0.18	0.51	0.50	0.24	0.07	0.31	0.32

If we make the further assumption that there is no significant variation with solvent in the ratios in which the intermediates (I) and (II) partition between different paths in their reactions with the same nucleophile, then from the amounts of 3-chloro-2-iodopropan-1-ol formed by migration, the amounts of the other two isomers may be predicted for the dioxan-water mixtures. The comparison is shown in Table 3.

The observed results and calculated values are in good agreement, and in our view show that this method of describing the course of the reaction is a reasonable approximation. In view of the experimental uncertainties, however, it may well be that there is a small variation also in the partition-ratio for intermediate (I), as was observed for the corresponding intermediate in the addition of hypochlorous acid to allyl bromide.<sup>1</sup>

From these results and those in previous papers<sup>1,2</sup> the percentage of the total addition-products which can be regarded as derived directly from the initially formed intermediate (*e.g.*, I) can be compared for additions of hypochlorous acid to allyl chloride, allyl bromide, and allyl iodide in water. The values are, respectively, 94%, 60%, and 32%. The remaining addition can be thought to proceed through a rearranged intermediate (*e.g.*, II), and the amount increased substantially with increasing neighbouring-group participation of the allylic halogen atom, as would be expected provided that the rate of nucleophilic attack on the initial intermediate is similar in all cases.

It is interesting also to calculate, on the hypotheses that we have adopted, the ratios in which intermediates to which we must on this model ascribe structure (III) undergo attack by water in the 1- and 2-positions. The comparisons are given in Table 4.

TABLE 4.  
Ratios of attack by water at C<sub>(1)</sub> and C<sub>(2)</sub> in intermediates of type (III).

Substituents in (III)·		Nucleophilic attack by H <sub>2</sub> O (%)		Ratio C <sub>(1)</sub> : C <sub>(2)</sub>	Ref.
Hal <sub>a</sub>	Hal <sub>b</sub>	C <sub>(1)</sub>	C <sub>(2)</sub>		
Br	Cl	73	27	2.70	1
Cl	Br	70	30	2.33	1
Cl	Cl	69	31	2.22	2
Br	Br	80	20	4.00	14
I	Cl	71	29	2.45	This paper
Cl	I	68	32	2.17	This paper

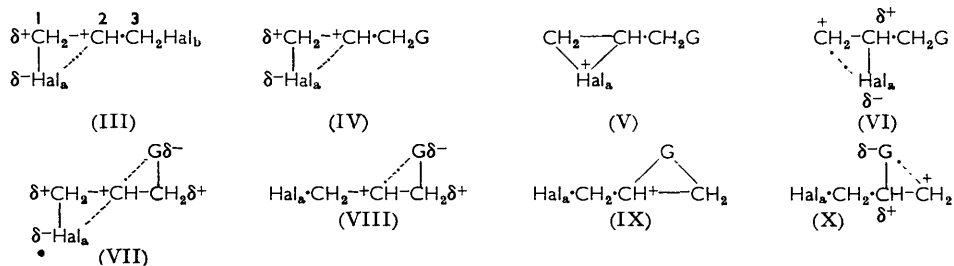
It is difficult to discern any trend in the partition ratio either with the halogen in control of the carbonium ionic centre or with the other halogen present; the similarity of the ratios for all the above intermediates is very striking and may be contrasted with the much larger differences observed when the allylic substituent is still further changed.<sup>7</sup> Thus, for (IV; Hal<sub>a</sub> = Cl), we have G = Cl, 2.22; G = Br, 2.33; G = I, 2.17; G = OH, 0.37; G = H, 0.19.

It should be emphasised that we do not consider the above formalisation of the reaction path to be the only way in which the experimental facts could be rationalised.

<sup>14</sup> Smith and Skyle, *Acta Chem. Scand.*, 1950, **4**, 39.

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In describing these reactions, we have a considerable choice of intermediates, even if we neglect the possibility of ion-pairing, complexing with the nucleophile, and formation of  $\pi$ -complexes. The three structures IV, V, and VI all need to be considered as possible independent intermediates for a non-rearranging reaction; for a rearranging reaction we need to consider also structures (VII)—(X).



In our discussion of the allyl halides we have neglected primary carbonium ions of the types (VI) and (X) for two reasons. First, because hydrogen chloride adds to allylic halides with exclusive attack by hydrogen at the carbon-1. Secondly, because the formation of (VI) directly from the olefin would not help in leading either to the rearranged or to the secondary alcohol. Since both of these can be major components of the reaction, it seems unlikely that much addition to allyl halides can proceed through such intermediates as (VI), though it is not excluded that a little of the primary unrearranged alcohol is formed in this way, as was proposed by Swindale, Swedlund, and Robertson.<sup>15</sup>

We have also neglected halonium and related structures of type (V) and (IX). Our reasons for doing so for attacking chlorine were set out in Part II;<sup>7</sup> we thought that, if they were first formed, they would ring-open with nucleophiles to give nearly exclusively the primary alcohol, whereas the secondary alcohol is also formed. As we pointed out in Part V, however,<sup>13</sup> there is more reason to believe in their participation for bromine and for iodine, and it seems to us that there is no cogent reason, except that of simplicity, for not including them also as extra intermediates in reactions in which these halogens are involved.

Symmetrical migrations, such as we described in Parts I and II, can also conveniently be considered as proceeding through an intermediate such as (VII), but we have not adopted this formulation for the unsymmetrical reactions, and now think it better to regard such a structure as a transition state separating two other intermediates, rather than as a true intermediate, particularly where one of the groups concerned is chlorine.

It should also be realised that there is no reason to be sure that the species which undergo reaction always react with solvent when at a point of energy-minimum in the reaction co-ordinates which allow interchange through the range (IV)—(VII). Sometimes, perhaps reaction with solvent can occur while the halogen atoms are moving, in which case such a precise description as is used for convenience in the Scheme would not be appropriate.

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<sup>15</sup> Swindale, Swedlund, and Robertson, *J.*, 1950, 812.