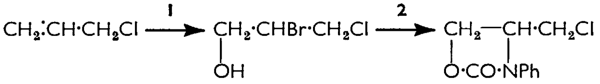
84. *The Kinetics and Mechanisms of Additions to Olefinic Substances. Part VIII.*[1] *Addition of Hypobromous Acid to Allyl Chloride, and of Hypochlorous Acid to Allyl Bromide.*

By P. B. D. DE LA MARE, P. G. NAYLOR, and D. L. H. WILLIAMS.

The preparation and properties of pure 2-bromo-3-chloropropan-1-ol and 3-bromo-2-chloropropan-1-ol have been recorded for the first time. The reaction of hypobromous acid with allyl chloride in the presence of perchloric acid gives a mixture containing 2-bromo-3-chloropropan-1-ol (73 ± 1%), 1-bromo-3-chloropropan-2-ol (26 ± 1%), and 3-bromo-2-chloropropan-1-ol ($\not>$0·8%). The corresponding reaction of hypochlorous acid with allyl bromide gives these isomers in the proportions 28 : 32 : 40, respectively. These proportions are not much changed by carrying out the reaction in the presence of silver perchlorate; they are significantly changed by altering the solvent.

ADDITION of hypochlorous acid to allyl chloride [2,3] gives a mixture of primary and secondary dichloro-alcohols of which 1,3-dichloropropan-2-ol comprises 30%. A similar result is found for the reaction of hypobromous acid with allyl bromide; here, 1,3-dibromopropan-2-ol forms 20% of the product.[4]

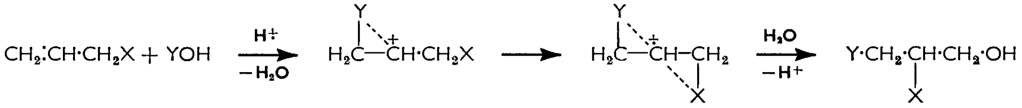
By analogy, it would be expected that the reaction of hypobromous acid with allyl chloride would give about 25% of 1-bromo-3-chloropropan-2-ol. This reaction has been investigated by Henry [5] and by Johnson and Langley,[6] who reported a single product, 2-bromo-3-chloropropan-1-ol, identified by conversion into (*a*) α-bromoacrylic acid and (*b*) 4-chloromethyl-3-phenyloxazolidin-2-one (I), identical with material prepared from 2,3-dichloropropanol:



$$CH_2{:}CH{\cdot}CH_2Cl \xrightarrow{1} \underset{\displaystyle OH}{\underset{|}{CH_2}}{\cdot}CHBr{\cdot}CH_2Cl \xrightarrow{2} \underset{\displaystyle O{\cdot}CO{\cdot}NPh}{CH_2\text{—}CH{\cdot}CH_2Cl} \quad (I)$$

1, BrOH. 2, Ph·NCO, then aq. KOH.

It seems most unlikely that this bromochloro-alcohol was in fact the sole product obtained by these workers. As far as we are aware, pure 2-bromo-3-chloropropan-1-ol has never been obtained before the present investigation; nor has its isomer, 3-bromo-2-chloropropan-1-ol. This might be expected as a minor component of the reaction mixture, through a rearrangement which may be written:



For X = Y = Cl, it has been shown [3] that about 4% of the product can be considered to be formed by migration of the allylic chlorine atom to the 2-position. When the attacking electrophile is bromine (Y = Br), one would expect the allylic chlorine (X = Cl) to compete less effectively, but it is interesting and important to establish whether or not it competes at all. To establish these matters has been the aim of the present investigation, of which a preliminary account has been given elsewhere.[7]

---

[1] Part VII, de la Mare, *J.*, 1960, 3823.
[2] Smith, *Z. phys. Chem.*, 1916, **92**, 729.
[3] de la Mare and Pritchard, *J.*, 1954, 3910, 3990.
[4] Smith and Skyle, *Acta Chem. Scand.*, 1951, **5**, 1415.
[5] Henry, *Ber.*, 1874, **7**, 757.
[6] Johnson and Langley, *Amer. Chem. J.*, 1910, **44**, 359.
[7] de la Mare, Naylor, and Williams, *Chem. and Ind.*, 1959, 1020.

EXPERIMENTAL

Some of the materials and methods have been described earlier.[3, 8, 9]

Infrared spectra were recorded on a Grubb–Parsons DB.2 double-beam grating spectrophotometer. Liquids were examined as thin films between rock-salt plates, solids in Nujol mull. Vapour-phase chromatograms were recorded on a Griffin and George instrument, with a 12″ × ¼″ column packed with kieselguhr and Silicone oil, and nitrogen as the carrier gas (1·5 l./hr.), at 154°; quantitative estimations were made by determining the areas under the appropriate curves; the estimations were checked by using samples of known composition.

Quantitative kinetic analysis of chlorobromo-alcohol mixtures were carried out by a procedure analogous to that adopted by de la Mare and Pritchard;[3] *ca.* 0·045M-reactants at 25° were used.

Radioactive measurements were determined by using standard equipment; results are expressed as counts $\text{min.}^{-1}\ \text{mole}^{-1}$, and have been corrected for background and where necessary for solvent.

Hypobromous acid was prepared from bromine, freshly precipitated silver phosphate, and water. It was distilled at 25—35° under reduced pressure before use. Allyl chloride had b. p. 45·5—45·8°/768 mm., n_D^{25} 1·4120; allyl bromide had b. p. 70·6—70·9°/755 mm., n_D^{25} 1·4658. Dioxan was purified as has been described elsewhere;[9] a solvent described as x% dioxan is one in which x ml. of dioxan had been mixed with $(100 - x)$ ml. of water.

A commercial sample of 1-bromo-3-chloropropan-2-ol was fractionally distilled (b. p. 83°/17 mm.). Its infrared spectrum is recorded in the Table; the most usefully diagnostic peaks are those at 664, 818, and 826 cm.^{-1}. The vapour-phase chromatogram showed one peak only, clearly separated from that of its isomers. Its reaction with alkali was very rapid at 25°.

2,3-Dibromopropan-1-ol was a commercial specimen. It was uniform in its behaviour with alkali, and gave only one peak in the vapour-phase chromatogram.

2-Bromo-3-chloropropan-1-ol.—Since epichlorohydrin is considered to react with nucleophiles under both acid and basic conditions[10] to give mainly secondary alcohol, an attempt was made to prepare this compound by the route: Epichlorohydrin $(+\text{AcOH–OAc}^-) \longrightarrow$ 1-Acetoxy-3-chloro-propan-2-ol $(+\text{PBr}_3) \longrightarrow$ 1-Acetoxy-2-bromo-3-chloropropane $(+\text{H}_2\text{O}) \longrightarrow$ 2-Bromo-3-chloropropan-1-ol. Although we obtained in reasonable yield an acetoxychloropropanol which appeared to have properties in accord with those reported for this isomer obtained similarly,[11] the final product was, from its infrared spectrum, entirely 1-bromo-3-chloropropan-2-ol, showing either that the acetate had been obtained with ring-opening in the sense opposite to that expected, or that rearrangement had occurred during the subsequent reactions. The following method was therefore adopted.

To allyl chloride (5 ml.) in 0·02M-aqueous perchloric acid (3·5 l.) was added *ca.* 0·12M-aqueous hypobromous acid (300 ml.) in 50 ml. portions during *ca.* 1 hr. The procedure was repeated by dissolving a further 5 ml. of allyl chloride in the solution, followed by adding a further 300 ml. of hypobromous acid. After a second repetition, the mixture was left for 24 hr. It was then saturated with ether and with sodium sulphate and extracted with ether. The ether extract was dried and fractionally distilled. There were obtained 18 g., b. p. 80—83°/20 mm., containing (vapour-phase chromatographic analysis) *ca.* 25% of 1-bromo-3-chloropropan-2-ol. This material was allowed to react with aqueous sodium hydroxide in slight excess over the 1-bromo-3-chloropropan-2-ol present. The material recovered in the usual way still contained a little 1-bromo-3-chloropropan-2-ol, so the procedure was repeated. There were recovered 5·4 g. of ***halide***, b. p. 83—84°/18·5 mm. (Found: C, 21·0; H, 3·6; Hal, 67·5; C_3H_6BrClO requires C, 20·8; H, 3·5; Halogen, 66·6%). The infrared spectrum is recorded in the Table; it had diagnostic absorption bands at 917, 746, and 718 cm.^{-1}, and the bands characteristic of the isomers were absent. Vapour-phase chromatography gave complete separation from 1-bromo-3-chloropropan-2-ol, but not from 3-bromo-2-chloropropan-1-ol. The reaction with alkali was too fast to measure very satisfactorily at 25° ($k_2 = ca.$ 9 l. $\text{mole}^{-1}\ \text{min.}^{-1}$) and showed that not more than about 0·5% of 3-bromo-2-chloropropan-1-ol was present.

---

[8] de la Mare and Galandauer, *J.*, 1958, 36.

[9] de la Mare and Harvey, *J.*, 1956, 36, 131.

[10] Boyd and Marle, *J.*, 1908, **93**, 839; Smith and Skyle, *Acta Chem. Scand.*, 1950, **4**, 39; Winstein and Goodman, *J. Amer. Chem. Soc.*, 1954, **76**, 4368.

[11] Knoevenagel, *Annalen*, 1914, **402**, 134.

Infrared spectra (cm.$^{-1}$; 620—1450 region) of isomeric bromochloropropanols.

1-Bromo-3-chloropropan-2-ol				2-Bromo-3-chloropropan-1-ol				3-Bromo-2-chloropropan-1-ol			
637w	861w	1064s	1256m	628m			1276w	621s	868w		1261m
664m	878w	1083s	1290m		850w	1087m		678w			1299w
709m			1342w	718s	904w	1098m	1326w	702m	901m	1096m	1326w
730w	930w	1129m	1379m	746w	917w	1149m	1381w			1143w	1361w
757m	952w	1189m	1422s		964m	1176w			969m		1387w
818m	990w	1220m			1015m	1233m	1427m		1015sh	1200m	1420m
826sh	1038s	1229sh			1050s		1439w	847w	1043s	1221m	1449m

The following are details of a kinetic measurement at 0°, with bromochlorohydrin and sodium hydroxide both initially 0·0440M; samples (5·0 ml.) were added to an excess of standard acid and back-titrated with alkali. The slightly falling velocity coefficient is such as to indicate that the sample still contained about 4% of 1-bromo-3-chloropropan-2-ol.

Time (min.)	0·0	6·25	14·0	26·0	41·0	51·0	61·0	76·0	∞
Titre (ml. 0·022M-NaOH) ...	2·25	3·33	4·26	5·27	6·19	6·69	7·07	7·55	11·20
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·56	0·53	0·51	0·49	0·49	0·49	0·49	—

Under the same conditions, 2,3-dibromopropan-1-ol had k_2 = 0·47 l. mole^{-1} min.$^{-1}$.

2-Bromo-3-chloropropanol gave a *triphenylmethyl ether* by the following procedure. The alcohol (0·6 g.) was dissolved in dry pyridine (5 ml.), and recrystallised triphenylmethyl chloride (1 g.) was added. The mixture was boiled under reflux for *ca.* 5 min., then poured on ice. On being stirred, the precipitated oil solidified. Recrystallised from aqueous ethanol, it had m. p. 97° (Found: C, 63·3; H, 4·9; Hal, 28·2. $C_{12}H_{20}OBrCl$ requires C, 63·5; H, 4·8; Hal, 27·8%).

3-Bromo-2-chloropropan-1-ol.—Allyl bromide (200 ml.) was added during 3 hr. to *ca.* 0·25M-aqueous hypochlorous acid (8 l.). After 24 hr. the product was recovered as usual, being a mixture of bromochloropropanols (230 g.; b. p. 78—83°/17 mm.) containing by kinetic analysis *ca.* 40% of the 2-chloro-isomer. This, of the isomeric bromochloropropanols with which we are concerned, is the least reactive with alkali, so the product was treated with M-aqueous sodium hydroxide (1400 ml.) for 10 min. at 0°. Recovery gave 89 g. of bromochloropropanols, b. p. 90—93°/20 mm. This material, by kinetic analysis, contained 82% of the 2-chloro-isomer. The enriched product was treated again with a slight excess of alkali for 20 min. at 0°. Recovery gave 45 g., and the b. p. 86·5—87·5°/17 mm. (Found: C, 21·3; H, 3·6; Hal, 65·8%). The infrared spectrum of this *product* is recorded in the Table. It had diagnostic absorption bands at 847 and 621 cm.$^{-1}$. Vapour-phase chromatography showed that 1-chloro-3-bromopropanol was absent, but did not separate 2-bromo-3-chloro- from 3-bromo-2-chloro-propan-1-ol. The following shows its rate of reaction with alkali. To 0·0461M-sodium hydroxide (100 ml.) was added an equivalent amount (0·7985 g.) of 2-chloro-3-bromopropan-1-ol. At intervals, samples (10 ml.) were added to 0·0500M-acid (10 ml.) and back-titrated with 0·0461M-sodium hydroxide, Bromocresol Green–Methyl Red being used as indicator. The mean value of the velocity coefficient is 0·297 l. mole^{-1} min.$^{-1}$; the corresponding value at 0° is 0·011 l. mole^{-1} min.$^{-1}$. The kinetic data show that the sample contains about 3% of faster-reacting material, probably 2-bromo-3-chloropropanol.

Time (min.)	0	5·0	10	15	25	40	60	83	105	1200	∞
Titre (ml.)	0·90[a]	1·78	2·32	2·76	3·54	4·47	5·42	6·20	6·29	10·80	10·8
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·424	0·360	0·336	0·316	0·306	0·304	0·301	0·305	—	—
k_2 * (l. mole^{-1} min.$^{-1}$)	—	—	0·306	0·293	0·292	0·292	0·296	0·296	0·300	—	—

* When t = 5·0 is taken as " zero time." [a] Calc., 0·77.

The *triphenylmethyl ether*, prepared as was described for the isomer, had m. p. 80° (Found: C, 64·3; H, 5·0; Hal, 27·0%). The slightly high value for carbon was not improved by recrystallisation or by chromatography on alumina.

Reaction of Hypobromous Acid with Allyl Chloride.—The reaction was carried out as described for the preparation of 2-bromo-3-chloropropan-1-ol, with a total of 850 ml. of 0·08M-hypobromous acid. A product was recovered (8·9 g., 77% yield) having b. p. 81—84°/19 mm. (Found: C, 21·1; H, 3·6; Hal, 66·3. Calc. for C_3H_6BrClO: C, 20·8; H, 3·5; Hal, 66·6%). From this was obtained by the usual procedure the triphenylmethyl ether, m. p. 97°, of 2-bromo-3-chloropropan-1-ol. Vapour-phase chromatography showed that the mixture contained

27 ± 1% of 1-bromo-3-chloropropan-2-ol, and this value was confirmed by determination on mixtures of known amounts of 1-bromo-3-chloropropan-1-ol with the isolated product.

The reaction was carried out also (a) in 40% and (*b*) in 70% dioxan, each 0·02N in perchloric acid. The products contained 26·5% and 26·2%, respectively, of 1-bromo-3-chloropropan-2-ol and so the change in solvent from water to 70% dioxan has very little effect on the product-composition. A mean value, 73 : 27, for the ratio of 3-bromo-2-chloropropan-1-ol to 1-bromo-3-chloropropan-2-ol is adopted in the Discussion.

Kinetic analysis did not detect with certainty the presence of any 3-bromo-2-chloropropan-1-ol. However, the amount of this material was determined by using the method of isotopic dilution. Radioactive allyl chloride ($CH_2{:}CH{\cdot}CH_2{}^{36}Cl$; activity 28,180 c. min.$^{-1}$ mole^{-1}; 3·0 g.) was allowed to react in aqueous perchloric acid with 0·0713M-hypobromous acid (450 ml.). The mixed product was isolated as usual, and to a portion (2·12 g.) was added inactive 3-bromo-2-chloropropan-1-ol (4·61 g.). From the mixture the triphenylmethyl ether, m. p. 80°, was prepared and recrystallised from pentane; each successive crystallisation markedly reduced the specific activity until after nine recrystallisations, 0·28 g. in 10 ml. of benzene gave a count of 6·0 per min. (after correction for background). This corresponds to the presence of 0·7 ± 0·1% of 3-bromo-2-chloropropan-1-ol in the reaction mixture; two further recrystallisations gave values of 0·65 ± 0·15% and 0·62 ± 0·3%: the value is constant within the statistical error, but not enough was left to ensure that the value would not be further reduced by recrystallisation.

A similar experiment was performed with allyl chloride and bromine chloride in 0·5M-aqueous hydrochloric acid. The chlorine in all the components of the mixture was adjusted to have the same radioactivity. Bromodichloropropanes were removed from the product by extraction with pentane. The bromochloropropanols were then recovered and analysed by isotopic dilution. The progress of the recrystallisation of the triphenylmethyl ether of 3-bromo-2-chloropropan-1-ol was very similar to that of the previous experiment and showed that not more than 0·7 ± 0·1% of 3-bromo-2-chloropropan-1-ol was produced in the reaction.

The bromochloropropanol fraction from reaction between allyl chloride and bromine chloride in aqueous hydrochloric acid was also analysed by vapour-phase chromatography and by infrared spectroscopy. Only 1-bromo-3-chloropropan-2-ol and 2-bromo-3-chloropropan-1-ol were found; the proportions were the same as for the reaction with hypobromous acid and were unchanged by change in concentration of hydrochloric acid over the range examined.

Reaction of Hypochlorous Acid with Allyl Bromide.—The procedure was essentially as described above. The isolated products always gave satisfactory analyses for elements and for halogenohydrin. Analysis specifically for 1-bromo-3-chloropropan-2-ol was by vapour-phase chromatography, for 3-bromo-2-chloropropan-1-ol by kinetic analysis, and for 2-bromo-3-chloropropan-1-ol by difference. The infrared spectra were carefully examined to confirm the presence, and approximately the proportion, of the third isomer; they, and the infrared spectra of synthetic mixtures of the pure isomers, confirmed the recorded proportions. The following Table gives the results.

Product analyses for reaction of hypochlorous acid with allyl bromide at 20°.

Solvent	$HClO_4$ (M)	$AgClO_4$ (M)	Yield (%) of mixed bromochloropropanols	Isomeric proportions of bromochloropropanols		
				1-Br-3-Cl	3-Br-2-Cl	2-Br-3-Cl
H_2O	0·02	—	74	32	40	28
40% Dioxan	0·02	—	43	37	45	18
70% Dioxan	0·02	—	51	39	50	11
H_2O	0·1	0·02	75	30	39	31
H_2O	1·0	0·02	70	30	39	31
H_2O	3·0 *	0·02	70	29	39	32

* In this experiment the product contained some impurity which was removed by dissolving the mixture in water and recovering the bromochloropropanols in the usual way.

The possibility of reversible exchange by the reaction $CH_2{:}CH{\cdot}CH_2Br + ClOH \rightleftharpoons CH_2{:}CH{\cdot}CH_2Cl + BrOH$ was examined in the following way. Radioactive hypochlorous acid ($HO^{36}Cl$) (250 ml., 0·085 mole) was added in portions (50 ml.) in 1½ hr. to an aqueous solution (3½ l.) containing allyl bromide (5 ml.) and perchloric acid (to 0·5M), the mixture being shaken after each addition. Further 5 ml. portions of allyl bromide were dissolved in the mixture after 100 ml. and 200 ml. of the hypochlorous acid had been added. After 24 hr., inactive allyl chloride (4·7 g.) was added to the reaction mixture, which was stirred until it was homogeneous. Air was then bubbled through the solution, and volatile material was condensed from the air-stream and fractionally distilled. Allyl chloride, b. p. 46°, n_D^{25} 1·417, was obtained; its radioactivity, under conditions in which the original hypochlorous acid had 16,000 c. min.$^{-1}$ mole^{-1}, was 63 c. min.$^{-1}$ mole^{-1}. This small activity is probably the result of contamination; it corresponds with the formation of, at the most, 0·02 g. of allyl chloride under conditions in which 10 g. of allyl bromide had undergone reaction.

Reactions of Bromochlorohydrins with Alkali.—From 3-bromo-2-chloropropan-1-ol (6·1 g.) in 0·045M-sodium hydroxide (1 l.), after reaction at 25° for 60 hr., epibromohydrin (2 g., 42%) was obtained and characterised by its b. p. and infrared spectrum. The aqueous solution was free from bromide.

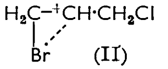
From 1-bromo-3-chloropropan-2-ol (58 g.) with an excess of 0·5M-sodium hydroxide was obtained pure epichlorohydrin (20 g., 65%), b. p. 114°, identified also by its infrared spectrum.

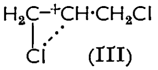
DISCUSSION

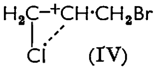
Reaction of Hypobromous Acid with Allyl Chloride.—The present work confirms the expectation that the reaction of hypobromous acid with allyl chloride should give some 1-bromo-3-chloropropan-2-ol. The amount found (26%) is very nearly that expected by analogy with the reactions of allyl chloride with hypochlorous acid and of allyl bromide with hypobromous acid.

The ratio is unchanged when the entering bromine is supplied as bromine chloride. Both these reactions are too fast for convenient kinetic measurement under the chosen experimental conditions, but the kinetic forms for the reaction of allyltrimethylammonium perchlorate with hypobromous acid[12] are analogous to those for the reaction of hypobromous acid with aromatic compounds,[9,13] and so it is presumed that we are concerned with electrophilic attack by Br^+ or $BrOH_2^+$ on the olefinic compound when no chloride is present, and of molecular bromine chloride when this is the bulk source of active halogen. Since this change in reagent is not associated with any noticeable change in product ratio, it seems probable that this ratio is determined in the present experiments from an intermediate (*e.g.*, II) in which the nucleophilic part of the halogenating species has substantially been removed.

We make the assumption, as in previous discussions,[3] that initial attack by the electrophile is on the terminal olefinic carbon atom. In the intermediate (II) concerned in the present reaction, neighbouring chlorine is available to compete with entering bromine, whereas in that (III) concerned in the reaction of hypochlorous acid with allyl chloride[3] chlorine competes with entering chlorine. In the latter reaction it was shown that some


$\underset{Br}{H_2C}{-}{}^{+}CH{\cdot}CH_2Cl$ (II)


$\underset{Cl}{H_2C}{-}{}^{+}CH{\cdot}CH_2Cl$ (III)


$\underset{Cl}{H_2C}{-}{}^{+}CH{\cdot}CH_2Br$ (IV)

8% of reaction could be considered as derived from a symmetrical intermediate, *i.e.*, that some 4% of the product was derived by migration of the chlorine already in the organic molecule from the 3- to the 2-position.[3] The corresponding figure in the present case is $\ngtr$0·8%. It is consistent with what is established about the relative efficiencies of bromine and chlorine in providing " driving force " for unimolecular substitutions[14] that chlorine should compete considerably less efficiently with bromine than with chlorine.

Reaction of Hypochlorous Acid with Allyl Bromide.—This reaction also, as would be

---

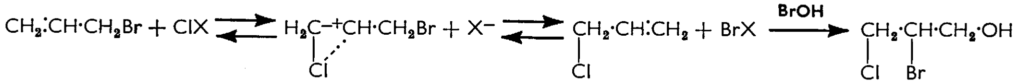
[12] Kanyaev, *Sbornik Statei obshchei Khim.*, 1953, **2**, 1172; *Chem. Abs.*, 1955, **49**, 5087.

[13] Shilov and Kaniev, *Compt. rend. Acad. Sci. U.S.S.R.*, 1939, **24**, 890; Derbyshire and Waters, *J.*, 1950, 564.

[14] Winstein and Grunwald, *J. Amer. Chem. Soc.*, 1946, **68**, 536; 1948, **70**, 828, 841, 846.

expected by analogy, gives a substantial amount of 1-bromo-3-chloropropan-2-ol. The proportion (30—40%) depends slightly on the conditions, as is discussed below.

The most notable feature of the present results, however, is that the reaction gives also a similar amount (in water, *ca.* 30%) of the rearranged 2-bromo-3-chloropropan-1-ol. We have excluded the possibility that this material arises by an exchange process, one possible mechanism of which involves reversibility of the initial attack by the electrophile:

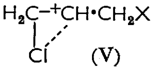


$$\mathrm{CH_2{:}CH{\cdot}CH_2Br + ClX \rightleftharpoons \underset{Cl}{H_2C}{-}{}^{+}CH{\cdot}CH_2Br + X^- \rightleftharpoons \underset{Cl}{CH_2}{\cdot}CH{:}CH_2 + BrX \xrightarrow{BrOH} \underset{Cl}{CH_2}{\cdot}\underset{Br}{CH}{\cdot}CH_2{\cdot}OH}$$

Further, in water the proportions are substantially unchanged by acidity, or by the presence of silver perchlorate. In the absence of silver perchlorate, reaction is much more rapid, and probably[3] involves molecular chlorine; in the presence of silver perchlorate, it is slower, and probably[3] involves $ClOH_2^+$ or Cl^+. So it seems that the nature of the electrophile is not much concerned in determining the product ratio, and hence the crucial intermediate probably has the stoicheiometry $[Cl^+,CH_2{:}CH{\cdot}CH_2Br]$, it being indeterminate whether solvent molecules are or are not covalently attached.

The product ratios show, therefore, that in such an intermediate, which we would formulate as (IV), the neighbouring bromine competes relatively effectively with chlorine for migration to the carbonium centre; some 30% of the product is obtained by migration of bromine to the 2-position. This also is consistent with the facts established[14] concerning the relative efficiency of bromine and chlorine in neighbouring group participation.

It is noteworthy that extent of migration and extent of participation are not directly related. The order[14] of relative efficiencies of participation is Br > OH > Cl; but it has been shown that, whereas chlorine certainly migrates less readily than bromine in these additions, the similarly placed hydroxyl group does not migrate at all.[3,15] Clearly the ease of heterolysis of the $CH_2{-}X$ bond in $CH_2{:}CH{\cdot}CH_2X$ is concerned in determining in part whether migration occurs in the cation (V).



$$\mathrm{\underset{Cl}{H_2C}{-}{}^{+}CH{\cdot}CH_2X}$$

(V)

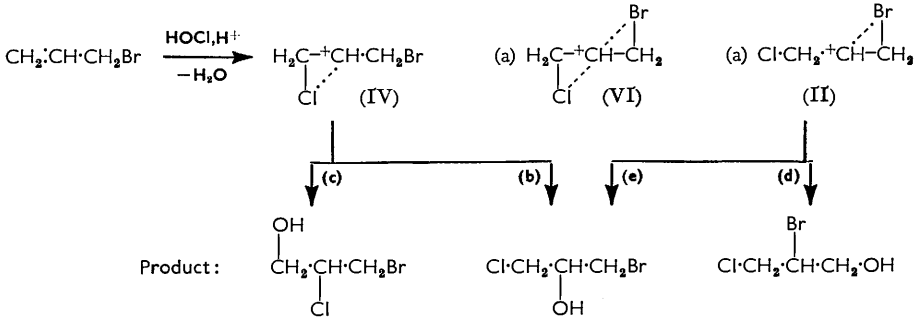
Solvent Variation.—The composition of the product of reaction of hypochlorous acid with allyl bromide changes significantly with change in solvent. The ratio of the non-rearranged bromochlorohydrins is very nearly constant (3-bromo-2-chloropropan-1-ol : 1-bromo-3-chloropropan-2-ol, in 3 experiments, 1·25, 1·21, 1·28); but the amount of rearrangement diminishes markedly, from 28% to 11%, as the ionising power of the solvent is decreased from water to 70% dioxan. This result is consistent with the view that the rearrangement to give 2-bromo-3-chloropropan-1-ol competes with the normal reaction (which itself gives a mixture) and does so more effectively in the more ionising solvent in which the intermediate carbonium ion can be considered to be more solvated and so to have a longer life.

For the reaction of allyl chloride with hypobromous acid, the product composition does not change appreciably with change in solvent from water to 70% dioxan. The simplest interpretation of the results for the two reactions seems to us to involve at least two carbonium ion species, which we may formulate as (II) and (IV). In the reaction of hypobromous acid with allyl chloride, intermediate (II) is produced in a conformation which approximates to its equilibrium structure; and its further reaction characteristically gives 73% of 2-bromo-3-chloropropan-1-ol and 27% of 1-bromo-3-chloropropan-2-ol (ratio, 2·70) with very little of the isomeric product of rearrangement. In the reaction of hypochlorous acid with allyl bromide (see Scheme), the structure (IV) approximately represents the species first formed, and this gives either (a) intermediate (II), which then gives its characteristic ratio of bromochloro-alcohols; or (b, c) the mixture of non-rearranged bromochloro-alcohols. The partition ratio for (II) can be assumed to be

---

[15] Winstein and Goodman, *J. Amer. Chem. Soc.*, 1954, **76**, 4638.

Possible routes and proportions of products in reaction of hypochlorous acid with allyl bromide.



In H_2O	40	21·6 + 10·4	28
In 40% dioxan	45	30·3 + 6·7	18
In 70% dioxan	50	34·9 + 4·1	11
Route:	(c)	(b) + (e)	(d)

constant (d : e = 2·70) and the same as that found for the reaction of hypobromous acid with allyl chloride in the same series of solvents. From this and the product composition we can determine by difference the various partition ratios for (IV). That which determines rearrangement [*i.e.*, a : (b + c)] is markedly solvent-dependent; it takes the values 0·62, 0·33, and 0·18 in water, 40% dioxan, and 70% dioxan, respectively. That which determines the proportions of non-rearranged products (c : b) is not so markedly dependent on solvent; it takes the values 1·85, 1·49, and 1·43, respectively.

The free-energy differences which determine these changes in proportions are small; the ratio 0·62 : 0·18 corresponds with a change in free-energy difference of 0·7 kcal. mole^{-1}, and that of 1·85 : 1·43 of only 0·1 kcal. mole^{-1}. The former is certainly significant; its direction corresponds with our view that the realisation of potential rearrangement depends on the lifetime of the cation, and that this is reduced by diminishing the ionising power of the solvent. The latter is too small to be regarded as experimentally validated; but its direction is such as to suggest that in solvents in which the cation has longer life the interaction between entering chlorine and developing carbonium ion centre has greater possibility of being established to full capacity.

The question whether such an ion as (VI), in which both halogens interact with a single carbonium ion centre, is an intermediate or merely a transition state between the two related structures (IV) and (II), is open, as is the question whether ion-pair intermediates are concerned in any, or in less ionising, solvents.

We thank Professor E. D. Hughes, F.R.S., and Professor Sir Christopher Ingold, F.R.S., for their interest, and the Department of Scientific and Industrial Research for maintenance grants to P. G. N. and D. L. H. W.

William Ramsay & Ralph Forster Laboratories,
University College London, Gower Street, London, W.C.1.
Bedford College, Regent's Park, London, N.W.1.
[*Received, September* 18*th*, 1961.]