8. *The Kinetics and Mechanisms of Addition to Olefinic Substances. Part V.* Products of the Reaction between Bromine Chloride and Propene in Water.*

By P. B. D. DE LA MARE and S. GALANDAUER.

Addition of bromine chloride to propene in aqueous hydrochloric acid gives 1-bromo-2-chloropropane and 2-bromo-1-chloropropane in the proportion 54 : 46. A mixture of bromohydrins is also produced, in amount decreasing as the amount of chloride ions is increased. This mixture contains 1-bromopropan-2-ol and 2-bromopropan-1-ol in the proportion 79 : 21. These ratios do not change significantly when the chloride-ion concentration is changed from 1M to 3M. There was no indication of the production of dichloride or of chlorohydrin. The theoretical significance of these results is discussed.

MICHAEL[1] first recorded that, when bromine chloride or iodine chloride is added to propene, significant amounts of the 2-bromo- or 2-iodo-isomers are produced. For

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* Part IV, *J.*, 1957, 1481.

[1] Michael, *J. prakt. chem.*, 1899, **60**, 450.

bromine chloride, it was recorded that the ratio of 1-bromo-2-chloropropane to 2-bromo-1-chloropropane was 58 : 42. This reaction was re-investigated by Stickler,[2] who gave a value of 80 : 20; his experimental details and conditions are not available to us.

For iodine chloride, Michael found the ratio of 2-chloro-1-iodopropane to 1-chloro-2-iodopropane to be 80 : 20. Ingold and Smith[3] repeated this estimation while studying orientation in such addition reactions, and obtained a value of 69 : 31.

The orientational and mechanistic significance attributable to the presence of the minor product of these reactions is obscured because the interhalogen compound might have acted as a donor of electrophilic chlorine rather than of bromine, *i.e.*, some reaction might have occurred through chlorine produced by the equilibrium $2BrCl \rightleftharpoons Cl_2 + Br_2$, or bromine chloride might have become polarised during the collision between the reactants in the sense $\overset{\delta+}{Cl}-\overset{\delta-}{Br}$. We have re-investigated this problem to examine these mechanistic possibilities.

EXPERIMENTAL

1-*Bromo*-2-*chloropropane*.—This was prepared by treating α-chloropropionic acid with thionyl chloride and reducing the α-chloropropionyl chloride with lithium aluminium hydride. The chlorohydrin, which was accompanied by much by-product of higher b. p., presumably a condensation product (*e.g.*, $Me{\cdot}CHCl{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}Me$), was brominated with phosphorus tribromide as recommended by Dewael;[4] the product (11% yield), repeatedly dried (P_2O_5) and distilled under reduced pressure, had b. p. 116—117°/760 mm., n_D^{25} 1·4740 (Found: C, 23·0; H, 3·9; Hal, 71·6 *. Calc. for C_3H_6ClBr: C, 22·8; H, 3·8; Hal, 73·1%).

The infrared spectrum is recorded in Table 1, together with those of related compounds, determined as thin films between rock-salt plates, by use of a Grubb-Parsons double-beam recording infrared spectrophotometer. Its isomer has characteristic peaks at 717 cm.$^{-1}$ and 741 cm.$^{-1}$, and these absorption bands do not appear, or at the worst appear only very weakly, in the spectrum of 1-bromo-2-chloropropane; thus the specimen was contaminated with less than 1—2% of the isomer.

2-*Bromo*-1-*chloropropane*.—Allyl chloride was treated with sulphuric acid, cupric sulphate, and water, the resulting chlorohydrin being brominated with phosphorus tribromide. The product (13% yield), repeatedly dried (P_2O_5) and distilled, had b. p. 116—117°/760 mm., n_D^{25} 1·4761 (Found: C, 23·4; H, 4·0; Hal, 73·2%). The infrared absorption spectrum (Table 1) shows that the specimen contained no isomeric bromochloropropanes, since absorption bands characteristic of the latter (*e.g.*, at 842, 671, 664, and 627 cm.$^{-1}$) are absent.

Analysis of Mixtures of 1-*Bromo*-2-*chloropropane and* 2-*Bromo*-1-*chloropropane*.—(i) *Infrared absorption*. The strong bands at 1151 cm.$^{-1}$ and 1163 cm.$^{-1}$, each characteristic of one isomer, appear in spectra of their mixtures as a double peak. Examination of mixtures containing 50—60% of the former isomer showed that the relative heights of the two peaks defined the composition to within about 0·5 unit per cent. This method was used, therefore for analysis of the products of reaction of bromine chloride with propene, as described below (Table 3).

(ii) *Kinetic methods*. The isomeric bromochloropropanes with sodium ethoxide in ethanol liberated acid at rates which were too similar for this method to be useful for kinetic analysis of mixtures, but rates of solvolysis in 50% ethanol were better separated. Samples of solutions in 50% ethanol (equal volumes of ethanol and water at room temperature) were sealed in tubes and heated at 99·9°. At intervals, the tubes were broken under ethanol containing perchloric acid, and the liberated halide ions titrated with silver nitrate potentiometrically, a silver wire being used as one electrode and a calomel half-cell as the reference electrode. Two end-points were obtained; the first, at 20—60 mv, represented liberation of bromide, and the second, at 220—260 mv, liberation of total halide. Values of the percentage of liberation of bromide,

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* Bromine and chlorine being assumed present in equal proportion.

[2] Stickler, personal communication to G. W. Wheland, " Resonance in Organic Chemistry," John Wiley and Sons, 1955, p. 455.

[3] Ingold and Smith, *J.*, 1931, 2752.

[4] Dewael, *Bull. Soc. chim. belges*, 1930, **39**, 87.

calculated on the basis of the theoretical infinity value, were plotted against time. Table 2 gives values obtained from such graphs.

Mixture B clearly contains more 1-bromo-2-chloropropane than does mixture S; this result (see Table 3) accords with the conclusion from infrared analysis. The first-order rate coefficients for the liberation of bromide, calculated on the above assumptions for the pure bromochloropropanes, were: 1-bromo-2-chloropropane, $k_1 = 4{\cdot}8 \times 10^{-5}$ min.$^{-1}$; 2-bromo-1-chloropropane, $k_1 = 18{\cdot}5 \times 10^{-5}$ min.$^{-1}$; these were substantially constant over 30—80% of reaction.

TABLE 1. *Infrared absorption bands (cm.$^{-1}$) of bromochloropropanes and of propylene bromohydrins.*

$Me{\cdot}CHCl{\cdot}CH_2Br$	$Me{\cdot}CHBr{\cdot}CH_2Cl$	$Me{\cdot}CH(OH){\cdot}CH_2Br$	$Me{\cdot}CHBr{\cdot}CH_2{\cdot}OH$
627 m	—	—	—
664 m	—	662 s	659 w
671 m	—	670 s	669 w
676 m	—	—	—
—	717 s	—	—
735 vw	741 m	—	—
—	—	792 w	—
842 w	—	821 m	—
857 w	859 w	858 w	858 w
893 m	871 w	873 m	879 w
—	878 w	—	892 w
905 m	900 m	935 s	915 w
986 m	—	978 w	978 m
993 m	998 s	—	—
1007 s	—	1033 s	1011 s
1034 m	—	1052 s	1028 s
1063 w	1063 s	1078 s	1057 s
1099 m	1106 w	—	1089 m
1117 m	1116 w	1134 s	1122 m
1171 s	1163 s	1190 m	1190 m
1220 s	1215 s	—	—
1227 s	—	1233 s	—
1245 m	1242 m	—	1250 m
1263 m	1264 m	1266 m	1263 m
—	1269 m	—	—
1309 m	1316 m	1300 m	1305 w
—	1335 w	1337 m	—
1372 s	1374 s	1381 s	1385 m
1416 m	—	—	—
1435 s	1431 s	1429 s	—
1443 s	1443 s	1458 m	1458 s
—	—	1650 w	—
2817 m	2825 m	2941 m	2941 s
2882 m	2882 m	2985 s	2976 m
2915 s	2933 s	3378 s	3344 s

s = strong; m = medium; w = weak; vw = very weak.

TABLE 2. *Hydrolytic liberation of bromide ions from bromochloropropanes in* 50% *ethanol at* 99·9°.

Liberation of Br^- (%)	20	30	40	50	60
$Me{\cdot}CHCl{\cdot}CH_2Br$; t (hr.)	85	150	200	270	320
$Me{\cdot}CHBr{\cdot}CH_2Cl$; t (hr.)	20	35	45	60	100
Mixture S *; t (hr.)	45	60	95	140	200
Mixture B *; t (hr.)	50	70	105	150	210

* S, Synthetic mixture, 50% of each isomer; B, sample from addition of bromine chloride to propene.

1-*Bromopropan*-2-*ol*.—Allyl bromide (140 g.) was added slowly to concentrated sulphuric acid (240 g.) containing copper sulphate (4 g.). The mixture was added cautiously to water and steam-distilled. The distillate was salted out with ammonium sulphate and extracted with ether. The ether-extract was dried over ignited silica gel. Fractional distillation gave 1-bromopropan-2-ol (50 g.), b. p. 48—48·5°/13 mm., n_D^{25} 1·4772 (Found: C, 25·7; H, 5·1; Br, 57·1. Calc. for C_3H_7OBr: C, 25·7; H, 5·0; Br, 57·0%) (for infrared spectrum see Table 1). Although the material so prepared should be free from the isomer, the spectra suggest that it contains a trace of it, as shown, for example, by a very weak band at 978 cm.$^{-1}$, corresponding with the much more intense band there of 2-bromopropan-1-ol. The latter is more reactive in solvolysis, and kinetic analysis confirmed that the specimen of 1-bromopropan-2-ol was 94 ± 1% pure, and contained 6% of a more rapidly solvolysing impurity.

*2-Bromopropan-*1-*ol.*—The product of α-bromopropionic acid and thionyl chloride was reduced with lithium aluminium hydride to 2-bromopropan-1-ol (cf. ref. 5), which (20% yield) had b. p. 145°/758 mm., 45°/12 mm., n_D^{25} 1·4740 (Found: C, 26·1; H, 5·2; Br, 56·8%) (for infrared spectrum see Table 1). It appears to be quite free from its isomer (absence of strong band at 935 cm.$^{-1}$, characteristic of 1-bromopropan-2-ol).

Analysis of Mixtures of 1-*Bromopropan*-2-*ol and* 2-*Bromopropan*-1-*ol.*—Kinetic analysis was satisfactory since the rates of hydrolysis at 100·2° in initially neutral solution in water differed by a factor of about seven. The rate coefficient for the hydrolysis of 2-bromopropan-1-ol was $k_1 = 35·5 \times 10^{-3}$ min.$^{-1}$. The best sample of 1-bromopropan-2-ol prepared gave the following behaviour, portions (5·64 ml.) being titrated at intervals with 0·02057N-sodium hydroxide.

Time (min.)	0	20	40	60	90	130	170
Titre (ml.)	0·31	3·61	6·40	8·85	11·40	14·52	17·16
$\log_{10}(A - x)$	1·433	1·378	1·323	1·270	1·205	1·144	1·016
10^3k_1 (min.$^{-1}$)	—	—	—	—	—	5·35	5·57

Time (min.)	210	260	320	380	460	∞
Titre (ml.)	19·05	21·28	22·80	23·91	25·51	27·45
$\log_{10}(A - x)$	0·924	0·794	0·668	0·549	0·288	—
10^3k_1 (min.$^{-1}$)	5·39	5·61	5·38	5·11	5·71	—

The quoted values of the first-order rate-coefficients, k_1, are calculated by the usual formula, with $t = 90$ min. as the zero of time. For a mixture of isomers in total concentration A, if $\log_{10}(A - x)$ is plotted against time t, a curve is obtained, of limiting slope towards the conclusion of the reaction $-k_1/2·303$, where k_1 is the first-order rate coefficient for the less rapidly reacting isomer. Extrapolation of the best straight line through the later points gives an intercept of $\log_{10}a$ on the $A - x$ axis, where a is the concentration of the less rapidly reacting isomer. This treatment gives the mean rate coefficient as $5·45 \times 10^{-3}$ min.$^{-1}$, and demonstrates that the above sample is about 94% pure. There is present, therefore, about 6% of a more rapidly reacting impurity, presumably its isomer. Similar kinetic treatment of a synthetic mixture, containing 74·3% of 1-bromopropan-2-ol, gave 75·0% for the proportion of the less rapidly reacting isomer. This good accordance confirms this method of analysis.

Addition of Bromine Chloride to Propene.—Bromine chloride was prepared by adding the theoretical weight (37·8 g.) of bromine to a standardised solution (4 l.) of chlorine in 1·0M-hydrochloric acid. Propene, from a cylinder kindly given by Imperial Chemical Industries Limited, whom we thank, was passed through this solution in a dark vessel until all the bromine chloride was destroyed. The bromochloropropanes were extracted with pentane, and the extract was dried ($CaCl_2$) and distilled. There were recovered 4·3 g. (5·8%) of mixed bromochloropropanes, b. p. 116—118°/760 mm., 31·5—32°/30 mm., n_D^{25} 1·4740 (Found: C, 23·4; H, 4·0; Hal, 71·5%). To the aqueous residue after extraction with pentane was added ammonium sulphate to salt out the organic material, and the mixture was then extracted with ether to give 37·9 g. (58%) of mixed bromohydrins, b. p. 141—143°/760 mm., 45·5—49°/12 mm., n_D^{25} 1·4752 (Found: C, 26·0; H, 5·4; Br, 57·4%).

This experiment was repeated at other acidities. In no experiment was there any sign of material corresponding in b. p. or refractive index with either 1 : 2-dichloropropane or chlorohydrin. The total recovery in the best example was greater than 60%.

Analysis of the proportion of bromohydrin produced in the reaction was carried out as follows. A standardised solution of bromine chloride was prepared in aqueous hydrochloric acid. Propene was passed slowly through it until it was colourless. The solution was carefully neutralised with aqueous sodium hydroxide, care being taken to avoid local excess of alkali, with methyl-red as indicator. This removed the excess of hydrochloric acid, together with the acid produced in the reaction. Excess of standard sodium hydroxide was then added, and the solution was left for some hours to destroy the bromohydrins. The solution was then back-titrated with hydrochloric acid. The following is a typical example. From a solution of bromine chloride (0·191M in 1·0N-hydrochloric acid), the bromohydrin liberated, on reaction with excess of alkali overnight, equalled 0·134N-acid. Hence 70% of bromohydrin is produced. Values for this and other experiments are given in Table 3, together with the results of analyses of the products isolated from the larger-scale experiments.

TABLE 3. *Products of reaction of bromine chloride with propene in aqueous hydrochloric acid.*

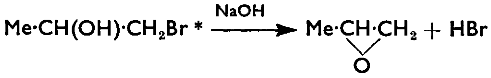
Concn. of HCl in reaction medium (M)	1·0	2·0	3·0
Bromohydrin formed (%)	70	60	51
1-Bromo-2-chloropropane in bromochloropropanes (%)	53·5	55	54
1-Bromopropan-2-ol in bromohydrins (%)	78·5	79	79

Bromo-olefins, which might have been formed by substitution, could have escaped detection in the recovery of the products, but separate experiments showed that these formed, at most, only a small proportion of the overall product. Propene was passed through a solution of bromine chloride in 0·050N-hydrochloric acid. At the end of the reaction, a portion (25 ml.) was titrated with 0·100N-alkali; the acid formed in the reaction, additional to the hydrochloric acid already present, was thus found to be 0·0177N. Excess of alkali was added, and after an appropriate time the mixture was back-titrated with acid; the bromohydrin had liberated 0·0162N-acid. The first figure represents the acid liberated by the two reactions:

$$\mathrm{Me{\cdot}CH{:}CH_2 + BrCl + H_2O \longrightarrow Me{\cdot}CH(OH){\cdot}CH_2Br\,^{*} + HCl}$$

$$\mathrm{Me{\cdot}CH{:}CH_2 + BrCl \longrightarrow Me{\cdot}CH{:}CHBr + HCl}$$

The second represents that liberated by the reaction:



$$\mathrm{Me{\cdot}CH(OH){\cdot}CH_2Br\,^{*} \xrightarrow{NaOH} Me{\cdot}\underbrace{CH{\cdot}CH_2}_{O} + HBr}$$

Hence, at most, the reaction which forms bromohydrin is accompanied by less than 10% of substitution. Repetition of the above experiment with added sodium chloride (1·7M) confirmed this conclusion.

DISCUSSION

It is a marked feature of these experiments that the amounts of 1-bromo-2-chloropropane and 2-bromo-1-chloropropane formed in the reaction between propene and bromine chloride are nearly equal. It is customary to consider electrophilic addition to such a compound as propene in terms of mechanisms involving carbonium-ionic intermediates, and there are various possibilities here.

Addition could possibly proceed by Scheme 1, interaction between the carbonium-ionic centre and the neighbouring halogen substituent being assumed but for the time being not formulated.

Scheme 1.

$$\mathrm{2BrCl \rightleftharpoons Br_2 + Cl_2}$$

$$\mathrm{Br_2 + Me{\cdot}CH{:}CH_2 \xrightarrow{-Br^-} Me{\cdot}\overset{+}{C}H{\cdot}CH_2Br \xrightarrow{+Cl^-} Me{\cdot}CHCl{\cdot}CH_2Br}$$

$$\mathrm{Cl_2 + Me{\cdot}CH{:}CH_2 \xrightarrow{-Cl^-} Me{\cdot}\overset{+}{C}H{\cdot}CH_2Cl \xrightarrow{+Br^-} Me{\cdot}CHBr{\cdot}CH_2Cl}$$

In the present example, this can be excluded as a route to 2-bromo-1-chloropropane,

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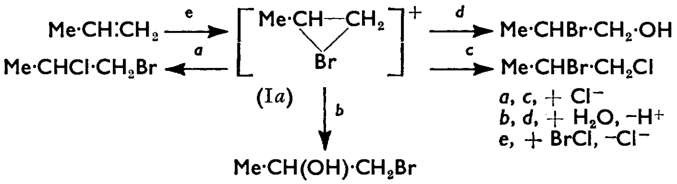
* And isomers.

for the concentration of chloride ion is so large, and so considerably exceeds that of bromide ion, that the final product of reaction through the cation $Me\cdot\overset{+}{C}H\cdot CH_2Cl$ would have to be 1 : 2-dichloropropane formed by attack of chloride ions in completion of the reaction.

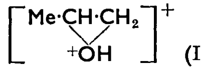
Similar considerations can be used to eliminate the possibility that 2-bromo-1-chloropropane is obtained by attack on the olefin by bromine chloride polarised in the sense $\overset{\delta+}{Cl}-\overset{\delta-}{Br}$, or by Cl^+. The formation of bromochloropropane clearly involves a diversion by chloride ions of a reaction which would otherwise have produced bromohydrin, for the yield of bromochloride becomes greater as the concentration of chloride ions is increased. Furthermore, increase in the concentration of chloride ions in the medium, though it increases the total amount of bromochloropropane produced, has no effect on the ratio of isomers isolated in this fraction. We conclude that the intermediate involved in the formation of bromochloropropane and of bromohydrin has the empirical composition $[(Me\cdot CH{:}CH_2), (Br)]^+$, and is obtained by attack on the olefin of a carrier of electrophilic bromine, not of electrophilic chlorine.

There remain a number of possible paths and intermediates. Scheme 2 gives a simple representation.

Scheme 2.



This scheme involves the formation of only one intermediate, which has been represented in the bromonium [6] form (I*a*)* This then reacts bimolecularly with chloride ions, or with water, to form the various products. It requires that there is an intrinsic difference in the ratios [(1 : 0·85 and 1 : 0·25)] in which chloride ions and water molecules respectively attack the primary and secondary carbon atoms of the intermediate (I*a*). Furthermore, the former ratio must be considerably different from that [7] of attack by the same reagent on the analogous cation (I*b*) (1 : 0·33).



(I*b*)

Elsewhere, however, arguments have been adduced [8, 9, 10] to suggest that more than one type of intermediate must be concerned in some of these reactions, as for example in the additions of halogens to cholesterol and its derivatives [11] and of hypochlorous acid to olefins. It would not accord with the experimental results to assume here that, whereas the 2-bromo-products were obtained as in Scheme 2, the 1-bromo-compounds were obtained wholly or partly by a unimolecular ring-opening of the bromonium ion (I*a*), followed by reaction with a nucleophilic reagent; for if the unimolecular ring-opening were partly rate-determining, in competition with stages (*c*) and (*d*) of Scheme 2, then increase in the concentration of chloride ions would divert the reaction towards stage (*c*), the formation of $Me\cdot CHBr\cdot CH_2Cl$, at the expense of all the other products, and so the ratio

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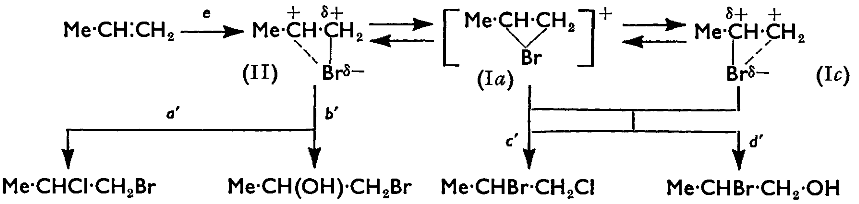
* It could equally be represented in the manner of (II), Scheme 3.

[5] Forsberg, *Acta Chem. Scand.*, 1954, **8**, 135.
[6] Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.
[7] Smith and Skyle, *Acta Chem. Scand.*, 1950, **4**, 39.
[8] de la Mare, in " Progress in Stereochemistry," ed. Klyne, Butterworths, London, 1953, p. 118.
[9] de la Mare and Pritchard, *J.*, 1954, 3910, 3679.
[10] Ballinger and de la Mare, *J.*, 1957, 1481.
[11] Grob and Winstein, *Helv. Chim. Acta*, 1952, **35**, 782.

of isomeric bromochloropropanes would alter with the concentration of chloride ions. This is contrary to experimental fact.

An elaboration of Scheme 2, which we prefer, is shown in Scheme 3, and accords with that suggested [8] for the addition of iodine chloride to propene.

Scheme 3.



In this scheme (route letters analogous to Scheme 2), at least two intermediates are envisaged: the unsymmetrical carbonium ion (II), stereochemically held in or near the indicated geometry by electrostatic forces; and either the bromonium ion (I*a*) or the other unsymmetrical carbonium ion (I*c*). The latter, if it exists as a kinetic intermediate, must be separated from (II) by (I*a*), which then might be either a true intermediate or a transition state.

These intermediates might be sufficiently stable to attain equilibrium, and then react at rates which for the various stages could be represented * as: (*a*′), $k_a . Cl^-$; (*b*′), k_b; (*c*′), $k_c . Cl^-$; (*d*′), k_d. The ratios $k_a : k_b : k_c : k_d = 1 : 4·4 : 0·85 : 1·1$ would then qualitatively reproduce the pattern of experimental results shown in Table 3, including the features that the total yield of bromochloropropane increases with increasing concentration of chloride ions, but that neither the ratio of isomeric bromochloropropanes nor that of the isomeric bromohydrins is altered by change in the concentration of chloride ions.

TABLE 4. *Proportion of product of attack on the* 1-*carbon atom in additions to olefins.*

Olefin	$Me·CH:CH_2$	$HO·CH_2·CH:CH_2$	$ClCH_2·CH:CH_2$	$BrCH_2·CH:CH_2$
ClOH; 1-chloro-compound in chlorohydrin (%) [7, 9]	91	73	30	—
BrOH; 1-bromo-compound in bromohydrin (%)	79 *	66 †	—	20 †
BrCl; 1-bromo-compound in bromochloride (%)	54	—	—	—
ICl; 1-iodo-compound in iodochloride (%) [3]	71	—	—	—

* Electrophilic reagent, BrCl; this paper. † Electrophilic reagent, BrOH; ref. 7.

It seems reasonable that intermediates (I) and (II) should differ in the ratios in which they react with chloride ions and with water, particularly should it turn out that the intermediate (I) is predominantly in the bromonium form (I*a*). Thus the fact that the ratio of isomeric bromohydrins is about 4 : 1 in favour of the 1-bromo-derivative, whereas that of the isomeric bromochloropropanes is much more nearly 1 : 1, is interpreted as showing the different nature of the two intermediates concerned in the addition.

In the corresponding earlier schemes [9, 10, 12] for addition of hypochlorous acid to olefins, equilibria involving intermediates analogous with (I*a*), (I*c*), and (II) are not fully established before other reactions of the ion set in. This does not introduce an inconsistency, for the facts known concerning the interaction between carbonium-ionic centres

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* It is implied that these values of *k* take into account the equilibrium constant between intermediates (I) and (II).

[12] de la Mare and Salama, *J.*, 1956, 3337.

and neighbouring halogen[13] suggest that the interaction is much more powerful with bromine than with chlorine, and hence the present example would be expected to be more favourable than those studied previously for the establishment of such equilibria.

The change in orientation with change in structure of the olefin, noted previously for the addition of hypochlorous acid,[9] is paralleled in the addition of hypobromous acid, as shown in Table 4.

The change in orientation with change from electrophilic chlorine to electrophilic bromine is also quite regular, but the sequence is apparently not continued regularly with iodine. Such a discrepancy does not seem to have a natural explanation in terms of Scheme 2, but it could be interpreted through Scheme 3; for the ratio of products formed by routes a' and c' will depend on both the ratio of the appropriate rate coefficients and the equilibrium proportions of intermediates (I) and (II). It would be consistent with current views on interaction between neighbouring groups and carbonium-ionic centres (cf. ref. 13) that the proportion of form (I*a*) in equilibrium with (II) might be greatest for iodine (sequence $I > Br > Cl$), but that, because of this difference in stability, the ratio of rates of further reaction of forms like (II) and (I*a*) might be least for iodine (sequence $I < Br < Cl$). Such a combination could give the irregular sequence of product-composition noted for propene in Table 4; we hope to investigate this further.

Added, November 4*th*, 1957.—Traynham and Conte[14] have recently described the preparation of 1-bromo-2-chloropropane by the chlorination, with thionyl chloride, of the bromohydrin produced by the reaction of hydrogen bromide with propylene oxide. They state that the infrared spectrum of their product was similar to that of 2-bromo-1-chloropropane except for a medium-intensity band at 9·05 μ (1105 cm.$^{-1}$) not found in the latter. Their procedure would be expected to give a mixture of these two isomers, since the corresponding reaction of propylene oxide with hydrogen chloride gives a mixture of chlorohydrins.[7] In our experience, the former compound is better distinguished by the bands at 1034 and 842 cm.$^{-1}$, the latter by the bands at 717, 741, and 1063 cm.$^{-1}$ (Table 1). Traynham and Conte do not describe their source of 1-chloropropan-2-ol, from which their 2-bromo-1-chloropropane was obtained; their spectrum, as far as they record it, accords qualitatively with that which we report for either isomer, their scale of wavelength being shifted with respect to ours by about +5 cm.$^{-1}$ These considerations clearly have relevance to their discussion of the possibility of migration of chlorine to the 2-position during the addition of hydrogen chloride to 3-chloropropene.

We are indebted to Dr. P. Ballinger for help with the infrared measurements and to Mr. C. Bilby for technical assistance. The continued interest of Professor E. D. Hughes, F.R.S., and of Professor C. K. Ingold, F.R.S., is greatly appreciated.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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[13] Cf. Winstein, *Bull. Soc. chim. France*, 1951, **18**, C55.

[14] Traynham and Conte, *J. Org. Chem.*, 1957, **22**, 702.