The Kinetics and Mechanisms of Addition to Olefinic Substances. Part I. Rearrangement accompanying Addition of Hypochlorous Acid to Allyl Chloride.

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Hypochlorous acid adds to allyl chloride at high dilutions in aqueous solution in the presence of perchloric acid and silver perchlorate to give a mixture of 1 : 3-dichloropropan-2-ol (30%) and 2 : 3-dichloropropan-1-ol (70%). Under the stated conditions, the kinetic measurements make it probable that the electrophilic reagent which initiates the addition is Cl^+ or H_2OCl^+. Previous workers have recorded similar proportions of the isomeric dichlorohydrins under conditions in which Cl_2 or Cl_2O are probably the functioning reagents. By using ^{36}Cl in the allyl chloride, it has been shown that a small proportion of the chlorine which is found in the 2-position of 2 : 3-dichloropropan-1-ol is derived by migration of the chlorine atom in the original allyl chloride. Approximately 88% of the 2 : 3-dichloropropan-1-ol must be derived from an intermediate which is not symmetrical about $C_{(2)}$. The significance of these observations is discussed.

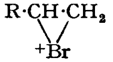
THE direction of addition to allyl chloride appears to vary considerably with the reagent. Even if reagents which add by free-radical reactions (*e.g.*, hydrogen bromide in the presence of peroxides) are neglected, the situation is still not immediately clear. Hydrogen chloride adds to form 1 : 2-dichloropropane, and hydrogen iodide gives 1-chloro-2-iodopropane (Kharasch, Kleiger, and Mayo, *J. Org. Chem.*, 1939, **4**, 430, 433; Kharasch, Norton, and Mayo, *J. Amer. Chem. Soc.*, 1940, **62**, 81). These results accord with the view that the CH_2Cl group releases electrons to an adjacent ethylenic system, an effect which would now normally be attributed to hyperconjugation. They also accord with the electron-releasing power of the CH_2Cl group, as shown in aromatic substitution by the predominantly *ortho-para*-directing character of the group, recently discussed by Ingold and Shaw (*J.*, 1949, 575) and by the greater reactivity (in *para*-substitution) of benzyl chloride than of benzene to electrophilic halogens (Swindale, Swedlund, and Robertson, *J.*, 1950, 812).

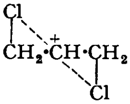
In the case of hypochlorous acid, on the other hand, it has been recorded that addition to allyl chloride gives predominantly 2 : 3-dichloropropan-1-ol, and this reaction was carefully investigated by Lennart Smith (*Z. physikal. Chem.*, 1918, **92**, 739). Using a kinetic method for the analysis of the product, he showed that the mixture of dichlorohydrins produced in the reaction contained about 70% of the 2 : 3-dichloro-compound. The latter result is clearly anomalous, since hypochlorous acid is generally considered to react in the sense $\overset{\delta+}{Cl}{-}\overset{\delta-}{OH}$, as is confirmed, for example, by addition of this reagent to propylene to give predominantly 1-chloropropan-2-ol.

An explanation of this difficulty has now been sought in the more detailed consideration of the course of addition of hypochlorous acid to allyl chloride. The attack of an electrophilic reagent, Cl–X, on an olefinic substance, $R\cdot CH{:}CH_2$, is often considered to proceed through the intermediate stage of a carbonium ion, $^+CHR\cdot CH_2Cl$. The fact that the completion of addition can be shown, by stereochemical observations in selected cases, to involve attack by a nucleophilic reagent on the side opposite from the attached halogen, is taken to imply interaction between the halogen and the carbonium ionic centre. Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, **59**, 947) suggested, for addition of bromine, that " bromonium " structures such as (I) contributed to the hybrid carbonium ions. Lucas and Gould (*ibid.*, 1941, **63**, 2541) wrote similar " chloronium " structures to explain *trans*-addition of chlorine to the isomeric but-2-enes.

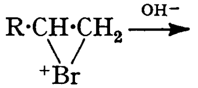
Similar intermediates are considered (cf. Winstein and Buckles, *ibid.*, 1942, **64**, 2787; Winstein and Grunwald, *ibid.*, 1948, **70**, 828) to be concerned in substitution reactions of 1 : 2-dihalides. The exact nature of these complexes has been a matter of some controversy (cf., for example, Winstein and Ingraham, *ibid.*, 1952, **74**, 1160), but this need not concern us for the moment. The crucial point is the possibility, which arises in any case of such interaction between a substituent and an adjacent carbonium centre, that subsequent reactions with nucleophilic reagents may occur in either of the two possible ways:

(I)





(II)



$R\cdot CH\cdot CH_2 \xrightarrow{OH^-} R\cdot CH(OH)\cdot CH_2Br$ and $R\cdot CHBr\cdot CH_2\cdot OH$. Furthermore, the symmetrical relation of the chlorine atoms in the similar intermediate (II) which might be derived from allyl chloride suggests that an experimental test of the intervention of an intermediate of this sort in the formation of 2 : 3-dichloropropan-1-ol from allyl chloride might be obtained by the isotopic labelling of the organic chloride.

In seeking the best experimental conditions for study of the reaction between hypochlorous acid and allyl chloride, we have been guided by kinetic considerations. The addition of hypochlorous acid to olefinic substances, under essentially neutral conditions, has been examined extensively by Shilov and his co-workers (cf. Shilov, Kupinskaya, and Yasnekow, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 435), as well as by Soper, Israel, and their co-workers (cf. Israel, Martin, and Soper, *J.*, 1950, 1282; Reeve and Israel, *J.*, 1952, 2327). The results indicate that the kinetic forms are extremely elaborate under these conditions. These complexities persist into more strongly acid conditions; but preliminary studies (de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 242) indicated that in very dilute aqueous solution, at pH less than 2, and in the presence of silver perchlorate to remove chloride ions, conditions exist under which Cl^+ and $ClOH_2^+$ are almost certainly the kinetic intermediates initiating the addition. These conditions have therefore been used in the present study, since in these circumstances an intermediate such as (II) is very likely to be involved.

EXPERIMENTAL

Materials.—Commercial allyl chloride was shaken with saturated aqueous potassium iodide, then with a little aqueous sodium nitrite, washed with water, dried, and fractionated, then having b. p. 44·4—44·7°, n_D^{25} 1·4120. To label this material with ^{36}Cl, the allyl chloride (100 ml.) was refluxed for 3 days with acetone and $Li^{36}Cl$, prepared from $H^{36}Cl$ obtained from a sample of $K^{36}Cl$ supplied by A.E.R.E., Harwell. The product was fractionated, and the material of b. p. 45—50° was washed repeatedly with ice-cold water to remove acetone, dried (Na_2SO_4), and fractionated, giving a material of b. p. 46°, n_D^{25} 1·4122.

Hypochlorous acid was prepared from chlorine water and mercuric oxide in the usual way (cf. de la Mare, Ketley, and Vernon, *J.*, 1954, 1290).

1 : 3-Dichloropropan-2-ol and 2 : 3-dichloropropan-1-ol were prepared as described elsewhere (de la Mare and Pritchard, *J.*, 1954, 1644). They were shown to be pure by kinetic

analysis; it is to be noted that this, as far as the authors are aware, is the only method so far established for estimating the purity of these isomeric compounds.

Reaction of Hypochlorous Acid with Allyl Chloride.—Allyl chloride (75 ml.) labelled with ^{36}Cl was dissolved in a solution (*ca.* 90 l., in a 100-l. flask) containing silver perchlorate (0·02M) and perchloric acid (0·02M). To this was added standardised 0·1M-hypochlorous acid solution (in total, 2·6 l.), at such a rate that the concentration of hypochlorous acid in the reaction mixture was always below 0·001M. On completion of the reaction, the excess of allyl chloride was removed by passage of air through the solution, and was then freed from acid by bubbling through saturated sodium carbonate solution, and from water by passage through anhydrous calcium chloride. The allyl chloride was then collected in traps cooled in liquid air.

The reaction mixture was saturated with ether (*ca.* 5 l.), and then with anhydrous sodium sulphate (*ca.* 14 kg.). The ether layer was removed, and the aqueous solution was further extracted several times (in total about 15 l. of ether). The ether extracts were dried (Na_2SO_4) and fractionated. After removal of the ether, there were obtained, with negligible intermediate fractions, (*a*) 1 ml., b. p. 70—81°/19·5 mm., which on redistillation at ordinary pressure gave *ca.* 0·1 g., b. p. 94—96°, n_D^{25} 1·4310 [the remainder (*ca.* 1 g.) distilled almost entirely over the range 176—182°], (*b*) 3 g., b. p. 81—82°/19·5 mm., n_D^{25} 1·4808, and (*c*) 12·5 g., b. p. 82—84°/19·5 mm., n_D^{25} 1·4815. Fractions (*b*) and (*c*) were combined for analysis as dichlorohydrin mixture (52% yield, based on the hypochlorous acid taken) (Found: C, 27·6; H, 4·9. Calc. for $C_3H_6OCl_2$: C, 27·9; H, 4·7%). This sample was also analysed kinetically, as discussed below, and contained 30% of 1 : 3-dichloropropan-2-ol and 70% of 2 : 3-dichloropropan-1-ol.

The dichlorohydrin mixture (15 g.) was allowed to react with 0·5N-sodium hydroxide (75 ml., being in excess by 8% of the amount of 1 : 3-dichloropropan-2-ol present) for 15 min. at 0°. The mixture was then extracted with ether, and the extract was dried (Na_2SO_4) and fractionated. After removal of the ether and epichlorohydrin, there were recovered 6 g. (60% recovery), n_D^{25} 1·4819, b. p. 85—86°/19·5 mm. (Found: C, 27·9; H, 4·8. Calc. for $C_3H_6OCl_2$: C, 27·9; H, 4·7%). Kinetic analysis then revealed, within the experimental error (*ca.* 1 unit %), no 1 : 3-dichloropropan-2-ol.

The above labelled 2 : 3-dichloropropan-1-ol (3·70 g.) was diluted with 8·04 g. of inactive, pure 2 : 3-dichloropropan-1-ol, and converted into epichlorohydrin by reaction with N-sodium hydroxide at 0° for 19 hr. The product was extracted with ether, and the extract was dried and fractionated, giving 2 g., b. p. 114—115°, together with some material of high b. p. (cf. de la Mare and Pritchard, *loc. cit.*). Refractionation gave pure epichlorohydrin (1·2 g.; b. p. 114—114·5°/760 mm., n_D^{25} 1·4358) (Found: C, 38·9; H, 5·7. Calc. for C_3H_5OCl: C, 38·9; H, 5·4%).

Known weights of the various samples were dissolved in alcohol and their radioactivity was determined by the technique usual for liquid samples (cf. de la Mare and Pritchard, *loc. cit.*). The results are shown in Table 1.

TABLE 1. *Counting data for samples from reaction of allyl chloride with hypochlorous acid.*

No.	Sample	Dilution ratio	Concn. of solution (g./10 ml.)	Mol. wt.	Count */ min.	Count/min. (corr. for mol. wt. and dilution)
1	Allyl chloride	1·00	0·6309	76·5	437·8	531 ± 5
2	Allyl chloride (recovered after reaction)	1·00	0·8155	76·5	566·8	532 ± 5
3	2 : 3-Dichloropropan-1-ol (recovered from reaction)	1·00	0·7342	129·0	310·8	546 ± 6
4	2 : 3-Dichloropropan-1-ol (diluted)	3·17	1·014	129·0	134·9	545 ± 8
5	Epichlorohydrin from 2 : 3-dichloropropan-1-ol	3·17	1·265	92·5	220·5	512 ± 7

* Counts are corrected for background (*ca.* 10 per min.). The probable errors are calculated on the basis of random fluctuations in the rate of counting. The first two results are strictly comparable, being done together; the next three are similarly comparable. The difference between samples 1—2, and 3—4 is probably slightly greater than the counting error, and probably results from a slight difference in counting conditions, since the two sets of counts were done at different times, and it is difficult to reproduce precisely the voltage-setting on the counter.

Kinetics of Addition of Hypochlorous Acid to Allyl Chloride.—This has been studied only in a very preliminary way, by the following method. Aqueous solutions of (i) allyl chloride and (ii) hypochlorous acid, perchloric acid, and silver perchlorate were mixed at 25° and transferred to a blackened flask (200 ml.), from which samples could be removed through a narrow, normally stoppered tube leading to the bottom of the flask. The latter was also attached to an aspirator (200 ml.) also containing the reacting solution at 25°; so that, when samples were removed for titration, the air replacing the removed solution was that in equilibrium with the reacting solution, and hence the concentration of reactants in the flask did not change appreciably as the result of volatility or diffusion losses. The samples were quenched in potassium iodide solution saturated with nitrogen, and were titrated under nitrogen with 0·001N-sodium thiosulphate, the starch–sodium glycollate indicator being used. The initial concentration of allyl chloride was determined by running a sample into a known excess of hypochlorous acid to which hydrogen chloride was added. The liberated chlorine reacted instantaneously with the allyl chloride, and the excess of chlorine was determined, after addition of potassium iodide, by back-titration in the usual way. The following are results at 25° for the reaction of 0·0085M-allyl chloride with 0·0044M-hypochlorous acid in the presence of 0·021M-perchloric acid and 0·020M-silver perchlorate; these conditions resemble closely those used in the product analyses.

Time (min.)	0·00	19·5	39·7	43·8	54·3	66·8	83·6	∞
Titre (ml. of 0·001N-$Na_2S_2O_3$)	5·62	4·63	3·90	3·65	3·27	2·88	2·50	0·00
10^3k_1 (min.$^{-1}$)	—	9·94	9·86	9·84	9·97	9·66	9·69	—

The reaction is clearly of the first order with respect to hypochlorous acid. If silver perchlorate is omitted, the reaction is very fast ($k_1 =$ *ca.* 1 min.$^{-1}$). Acid-catalysis is demonstrated by the following results, which apply to rather higher concentrations (*ca.* 0·02M) of allyl chloride, reacting with 0·0005M-hypochlorous acid in the presence of 0·02M-silver perchlorate: with 0·01M-$HClO_4$, $10^3k_1 = 16$ min.$^{-1}$; with 0·030M-$HClO_4$, $10^3k_1 = 33$ min.$^{-1}$.

Reaction of Allyl Chloride with Silver Perchlorate.—Silver perchlorate was added to the reaction mixture to minimise reaction through free chlorine. It was necessary to check, therefore, that silver perchlorate did not interfere with addition by catalysing hydrolysis of the allyl chloride. Below are the results obtained in following the decrease of concentration of silver ion at 25°, in a solution containing 0·02M-allyl chloride, 0·02M-silver perchlorate, and 0·01M-perchloric acid. Samples were used for titration, at intervals, potentiometrically, of 10·0-ml. samples of 0·0454N-sodium chloride.

Time (min.)	0·0	65	110	165	∞
Ag^+ (M)	0·0184	0·0180	0·0178	0·0175	0·0000
10^3k_1 (min.$^{-1}$)	—	0·35	0·32	0·32	—

The first-order rate-coefficient for the hydrolysis is less than 4% of the first-order rate-coefficient for the addition under the conditions used for the product analysis, and therefore the former reaction is considered to interfere negligibly with the latter.

Kinetic Analysis of Chlorohydrin Mixtures.—This aspect of the present study was greatly facilitated by the preliminary investigation by G. J. Pritchard and C. K. Ingold (personal communication). In a typical experiment, to 100 ml. of 0·04165M-alkali at 25° was added an exactly equivalent amount (0·5372 g.) of the mixed dichlorohydrins. At intervals, 10-ml. samples were added to 10 ml. of 0·0538N-hydrochloric acid, and back-titrated with 0·04165N-alkali. A correction was applied for the dilution of the solution by the added dichlorohydrin.

Time (min.)	0·0	4·6	16·2	34·9	56·1	100·9	123·6	∞
Titre (ml.)	2·90	6·03	6·72	7·49	8·15	9·22	9·60	12·84
$1/(a - x)$	0·1000	0·1468	0·1634	0·1869	0·2132	0·2762	0·3086	—

The expression for bimolecular reaction for pure single chlorohydrin is: $k_2 = x/(a - x)at$, or $1/(a - x) = k_2t + 1/a$. The plot of $1/(a - x)$ against t gives a straight line of slope k_2 and intercept $1/a$ on the $1/(a - x)$ axis. For a mixture of two compounds differing considerably in reaction rate, the plot of $1/(a - x)$ against t may be used to find the proportion of each compound present. Application of this treatment to the above data gives a straight line of slope $k_2 = 0{\cdot}32$ l. mole^{-1} min.$^{-1}$. This value agrees with that recorded elsewhere (de la Mare and Pritchard, *loc. cit.*) for pure 2 : 3-dichloropropan-1-ol. The intercept on the $1/(a - x)$ axis gives a value of $a = 0{\cdot}0292$ mole l.$^{-1}$. The ratio of a obtained by extrapolation and a calculated from the total weight of dichlorohydrin taken demonstrates that 70% of the starting material is 2 : 3-dichloropropan-1-ol. The remainder is isomeric 1 : 3-dichloropropan-2-ol, which is about 200 times more reactive than its isomer and was therefore destroyed to the extent of at least 99% before the first experimental point was reached. Separate experiments at 0°, in which the reaction constant could be calculated, confirmed that the reactive material was the isomeric dichlorohydrin. Synthetic mixtures of dichlorohydrins, similar in composition to the above, were analysed and gave results which checked with their known compositions within 1%. This method depends for its accuracy on the fact that, of the two isomers, one is considerably more reactive than the other (*e.g.*, by a factor of about 100).

DISCUSSION

(a) *Kinetics of Addition of Hypochlorous Acid to Allyl Chloride.*—Elsewhere (de la Mare, Hughes, and Vernon, *loc. cit.*), preliminary evidence has been presented showing that hypochlorous acid may, under controlled kinetic conditions, add to olefinic substances by way of the chlorinium ion, Cl^+. The evidence was derived from the observation that, in the absence of chloride ions, hypochlorous acid adds to such compounds as allyl ethyl ether and allyl fluoride at a rate, which, though subject to acid catalysis, is nearly independent, at low concentrations, of the nature of the olefinic material and its concentration.

More recently, a detailed examination of the kinetically similar reaction between hypochlorous acid and aromatic substances (de la Mare, Ketley, and Vernon, *loc. cit.*) has thrown further light on the complex kinetic behaviour of these systems. Very low concentrations ($\not>$ M/1000-hypochlorous acid) must be used to prevent part of the chlorination proceeding through Cl_2O. The full kinetic form, at concentrations of aromatic compound large enough to remove Cl^+ as soon as it is formed, is found to be :

$$-\mathrm{d}[\mathrm{ClOH}]/\mathrm{d}t = k[\mathrm{ClOH}] + k'[\mathrm{ClOH}][\mathrm{H}^+] + k''[\mathrm{ClOH}][\mathrm{H}^+][\mathrm{ArH}]$$

in which the first two terms of the right-hand side are considered to represent the rate of heterolytic fission of ClOH and $ClOH_2^+$ respectively, giving Cl^+, and the last term the rate of attack of $ClOH_2^+$ on the aromatic compound.

A difficulty in interpreting the coefficient k'' arises because unsaturated compounds (including aromatic materials) form complexes with the silver ion which must be added to prevent reaction proceeding through Cl_2. This difficulty is more serious in the case of the reactions of the olefins with hypochlorous acid than for aromatic compounds, because on the whole the equilibria $A + Ag^+ \rightleftharpoons [A{\cdot}Ag]^+$ lie further to the right for the former class of substances. So far, a full kinetic investigation of the reactions of the olefinic substances in which we are interested has not been completed; but the preliminary data presented here show the following : (*a*) under the specified conditions (high dilution, Ag^+ present), the rate is always of the kinetic form $-\mathrm{d}[\mathrm{ClOH}]/\mathrm{d}t \propto [\mathrm{ClOH}]$; (*b*) with sufficiently high silver-ion concentration, the rate becomes substantially independent of this concentration; (*c*) the magnitudes of the rates are similar to those obtained for the analogous reaction of, *e.g.*, phenol (cf. de la Mare, Ketley, and Vernon, *loc. cit.*) ; (*d*) the reaction is catalysed by acids. Subsidiary experiments showed that the concomitant hydrolysis of allyl chloride, catalysed by Ag^+, is slow and affects negligibly the addition reaction.

It is concluded, therefore, in agreement with de la Mare, Hughes, and Vernon (*loc. cit.*) that addition of hypochlorous acid follows, under these conditions, the same general pattern as substitution of aromatic compounds by this reagent; and that, under the conditions used for the product analysis, Cl^+ and $ClOH_2^+$ both contribute to the initiation of the addition.

(b) *Products resulting from Addition of Hypochlorous Acid to Allyl Chloride.*—The silver-ion-catalysed hydrolysis of allyl chloride, leading to allyl alcohol and thence to monochlorohydrin, appears, from its measured rate, to contribute less than 4% to the measured process. We were unable to detect any of the possible products (*e.g.*, $CH_2Cl{\cdot}CH{:}CHCl$ or $CH_2{:}CCl{\cdot}CH_2Cl$) of unimolecular elimination through the carbonium ions (*e.g.*, $CH_2Cl{\cdot}{}^+CH{\cdot}CH_2Cl$ or ${}^+CH_2{\cdot}CHCl{\cdot}CH_2Cl$) which might be considered as possible intermediates in the addition process. The only ether-extractable material recoverable in identifiable quantity from the reaction was a mixture of dichlorohydrins. The total yield (*ca.* 50%) is considered satisfactory in view of the great dilution at which the experiment was necessarily performed.

Kinetic analysis of the mixture of chlorohydrins obtained in various experiments carried out by us and by other workers gave the results shown in Table 2.

The isomeric product ratio does not seem to vary greatly with the nature of the electrophilic reagent which is concerned in the rate-determining attack on the double bond. The formation of an excess of 2 : 3-dichloropropan-1-ol may be taken, therefore, to be characteristic of an addition in which Cl^+ is supplied by an electrophilic reagent, and the solvent then provides the hydroxyl group to complete the addition.

TABLE 2. *Products from addition of hypochlorous acid to allyl chloride in water.*

Allyl chloride (M)	ClOH (M)	$AgClO_4$ (M)	$HClO_4$ (M)	Probable reagent	2 : 3-Dichloropropan-1-ol (%) *	Ref.
0·01	0·001	0·02	0·02	Cl^+, $ClOH_2^+$	70	This work
0·001	0·001	0·02	0·02	$ClOH_2$, Cl^+	68·5	,,
ca. 1	0·1	0·0	*ca.* 0·02	Cl_2O, Cl_2	66·5	,,
0·001	0·001	0·0	0·05	Cl_2, Cl_2O	67·5	,,
Allyl chloride + hypochlorite					68	Lennart Smith (*loc. cit.*)
Allyl chloride + concentrated chlorine water				Cl_2, Cl_2O	68	Ingold and G. J. Pritchard (personal communication)

* Accuracy estimated as ±1%.

(c) *Addition of Hypochlorous Acid to* $CH_2{:}CH\cdot CH_2\cdot{}^{36}Cl$.—When considering the results of Table 1, the following points should be noted. The excess of allyl chloride, recovered after completion of the reaction, maintained in full its radioactivity. This shows that radioactive dilution of the product does not arise from some exchange between allyl chloride and the reactants in the solution. A corollary is that the stage in which the Cl^+ is added to $C_{(1)}$ to form a carbonium cation is not reversible, so that there is no need to consider the possible reversibility of formation of a symmetrical cation, $[Cl\cdot CH_2\cdot\overset{+}{C}H\cdot CH_2\cdot{}^{36}Cl]$. Secondly, the writers have shown (*loc. cit.*) that when $HO\cdot CH_2\cdot CHCl\cdot CH_2\cdot{}^{36}Cl$ is treated with alkali, the recovered epichlorohydrin retains, within experimental error, all the ${}^{36}Cl$. Hence the diminution in specific activity of the epichlorohydrin (Table 1) is not the result of extraneous exchange during working-up of the products.

We consider, therefore, that the results show that some exchange occurs during the addition, and hence that some of the 2 : 3-dichloropropan-1-ol comes by migration of ${}^{36}Cl$ to $C_{(2)}$ in an effectively symmetrical intermediate, $[Cl\cdot CH_2\cdot\overset{+}{C}H\cdot CH_2\cdot{}^{36}Cl]$, written here without specifying interaction between the chlorine substituents and the carbonium ionic centre. If all the reaction proceeded by this route, then the specific activity of the epichlorohydrin isolated from the 2 : 3-dichloropropan-1-ol would have fallen from 546 counts/min. to 273 counts/min. That the observed value was 512 counts/min. indicates that not more than 12% could have been formed through such an intermediate. The remainder must be derived by some other route.

The following conclusions may then be drawn : First, the " unusual " orientation in the reaction of hypochlorous acid with allyl chloride has been confirmed. Secondly, this orientation persists under conditions in which Cl^+ and $ClOH_2^+$ are almost certainly the rate-determining electrophilic reagents. Thirdly, a small but significant amount of the 2 : 3-dichloropropan-1-ol comes from an intermediate such as (II) (p. 3911) in which the entering and the already present chlorine substituents have become effectively equivalent. Fourthly, the major amount of the 2 : 3-dichloropropan-1-ol does not come from such an intermediate, or from any cation of life long enough to allow the two chlorine atoms to become equivalent, as, for example, in a process of dynamic equilibrium between two forms :

In the accompanying paper, these conclusions are amplified by comparison with data relating to reactions of hypochlorous acid with other olefinic substances, and to the reactions of three-membered ring-compounds and intermediates.

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