The Kinetics and Mechanisms of Addition to Olefinic Substances. Part II. Addition of Chlorine to Allyl Alcohol. The Intermediates involved in Electrophilic Addition Reactions.*

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The addition of chlorine to allyl alcohol in aqueous solution in the presence of chloride ions gives 2 : 3-dichloropropan-1-ol. Thus the hydroxyl substituent does not migrate to the 2-position in the course of the addition. The significance of this is considered in relation to the facts and theories concerning addition reactions.

IN the preceding paper, evidence was presented that when hypochlorous acid is added to allyl chloride some of the chlorine substituent already present in the molecule migrates to the 2-position in the product. The chlorine substituent is one of the least effective of those groups which, when β to a carbonium ionic centre, have the effect (Lucas and Gould, *J. Amer. Chem. Soc.*, 1941, **63**, 2541) of preserving the optical configuration at that centre by the formation of a bridged intermediate; at least, this is certainly so if participation of a substituent in this way is judged by the ability of the group to facilitate heterolysis (cf. Winstein, *Bull. Soc. chim.*, 1951, C 55; Winstein and Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2787; Winstein and Grunwald, *ibid.*, 1948, **70**, 828). It is of interest to consider the effect of other, more effective participating groups when they are similarly situated. Of

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* Part I, *J.*, 1954, 3910.

these, the hydroxyl group is one such, and so the addition of chlorine to allyl alcohol has a special interest.

General considerations suggest that the $CH_2{\cdot}OH$ group should release electrons rather more readily than does the CH_2Cl group, since the inductive electron-withdrawal by the chlorine substituent should be greater than that by the hydroxyl group. This is borne out by comparison of the relative reactivities of allyl alcohol and allyl chloride in electrophilic additions (Bythell and Robertson, *J.*, 1938, 179; Swedlund and Robertson, *J.*, 1945, 131). The data on orientation of addition to allyl alcohol are in agreement with this opinion. Hydrogen chloride gives 2-chloropropan-1-ol (Dewael, *Bull. Soc. chim. Belg.*, 1924, **33**, 504) though no quantitative study has been made of this reaction. By kinetic analysis, Lennart Smith *et al.* (Smith, *Z. physikal. Chem.*, 1918, **92**, 717; cf. Smith and Skyle, *Acta Chem. Scand.*, 1950, **4**, 39) showed that addition of hypochlorous acid to allyl alcohol gives 73% of 3-chloropropane-1 : 2-diol and 27% of 2-chloropropane-1 : 3-diol.*

In the present work, the addition of chlorine water to allyl alcohol has been studied. At high dilution and low temperature (cf. U.S.P. 2,711,023), the reaction gives mainly monochlorohydrins in the isomeric ratio indicated above, but in the presence of excess of chloride ions the reaction can be considerably diverted towards the formation of some dichlorohydrin. Kinetic analysis of the ether-extractable product shows that the latter is almost entirely 2 : 3-dichloropropan-1-ol. Thus no migration of the hydroxyl substituent to the central carbon atom has been detected.

Note Added in Proof.—Winstein and Goodman (*J. Amer. Chem. Soc.*, 1954, **76**, 4638) have recently provided evidence, generally in concordance with our findings, that the hydroxyl substituent does not migrate during the addition of ClOMe or BrOMe to allyl alcohol.

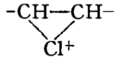
EXPERIMENTAL

A slight excess of chlorine was passed into a solution of allyl alcohol (25 ml.) in saturated aqueous sodium chloride (2 l.). The product was extracted with ether, and the extract was washed with sodium hydrogen sulphite solution and with water, dried, and fractionated. After removal of the ether, the following fractions were collected: (*a*) 2·1 g., b. p. 69—70°/9 mm., n_D^{25} 1·4823; (*b*) 4·3 g., b. p. 69°/9 mm., n_D^{25} 1·4820; (*c*) 6·8 g., b. p. 69°/9° mm., n_D^{25} 1·4820. The residue from column and still-pot gave on distillation 1 g., b. p. 180—190°, n_D^{25} 1·4820, and 2 g. of partly decomposed material of high b. p. Fractions (*b*) and (*c*) were bulked (20% yield) and subjected to kinetic analysis as follows. The dichlorohydrin (0·792 g.) was added at 0° to 0·0491N-sodium hydroxide (125 ml.), and at intervals samples (10 ml.) were pipetted into 0·0656N-hydrochloric acid (10 ml.) and back-titrated with 0·0491N-sodium hydroxide. The results were:

Time	0·00	69·7	101·9	150·7	209·3	271·1	305·6	∞
Titre (ml. of 0·0491N-NaOH)	3·32	3·66	3·83	4·05	4·24	4·52	4·67	13·36
10^2k_2 (l. mole^{-1} min.$^{-1}$)	—	1·02	1·06	1·05	1·03	1·01	1·03	—

The constancy of the rate coefficients, which agree with the value (10^2k_1 = 1·00 l. mole^{-1} min.$^{-1}$) recorded by de la Mare and Pritchard (*J.*, 1954, 1644) for 2 : 3-dichloropropan-1-ol, indicates the quantity of the isomeric dichlorohydrin, if present, to be less than 1%.

DISCUSSION



Since intermediates with three-membered rings, *e.g.*, as annexed, are customarily held to be concerned in addition reactions, it is necessary to consider comparatively the orientation of ring opening with that observed in addition processes. The following Tables summarise some of the available data.

The mechanisms involved in ring-opening of ethylene oxides have been much discussed, for example, by Ingold ("Structure and Mechanism in Organic Chemistry," G. Bell and

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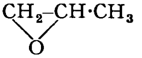
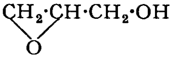
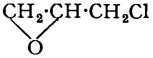
* The literature contains some misconceptions on this and related points. Israel, Martin, and Soper (*J.*, 1950, 1282) seem to have misread Smith's early work, which they quote as evidence that 2-chloropropane-1 : 3-diol is the major product; their theoretical account therefore requires reconsideration. Read and Hurst (*J.*, 1922, **121**, 996) state without conclusive evidence that, from the reaction of chlorine water and allyl alcohol, 2-chloropropane-1 : 3-diol is formed, no mention being made of the isomer; this clearly also needs revision in the light of Smith's findings.

Sons, London, 1953). It seems generally agreed that anion-catalysed ring openings involve nucleophilic attack on the oxide molecule, with, correspondingly, the expected orientation of attack at the primary position. The HCl-catalysed ring openings generally have the kinetic form $v \propto [\text{oxide}][H^+][Cl^-]$; on the whole, they preserve orientation involving nucleophilic attack at the primary carbon atom, and they are therefore considered to involve to a predominant extent nucleophilic attack on the oxonium cation (*A*). The proportion of the other isomeric product formed under acid conditions is thought to indicate partial reaction through the " open " " classical " carbonium cation; ring opening in this direction is facilitated by increasing electron release from the CH_2X group, as is exemplified in the horizontal comparisons of Table (b).

(a) *Percentage of nucleophilic attack on the central carbon atom in addition to* $CH_2{:}CH{\cdot}CH_2X$.

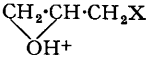
	Compound	$CH_2{:}CH{\cdot}CH_3$	$CH_2{:}CH{\cdot}CH_2{\cdot}OH$	$CH_2{:}CH{\cdot}CH_2Cl$
Reagent:	HCl	100 [a]	*ca.* 100 [b]	100 [a]
Reagent:	ClOH	91 [c]	73 [c]	30 [c, d]
Reagent:	ICl	70 [e]	—	—

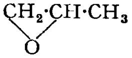
(b) *Percentage of nucleophilic attack on the central carbon atom in ring opening of substituted ethylene oxides.*

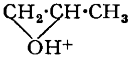
	Compound	 $CH_2{\cdot}CH{\cdot}CH_3$	 $CH_2{\cdot}CH{\cdot}CH_2{\cdot}OH$	 $CH_2{\cdot}CH{\cdot}CH_2Cl$
Reagent:	OR^-	2 [f]	0	0 [g]
Reagent:	HCl	25 [c]	10 [c]	0 [c]
Reagent:	$ROH-H_2SO_4$	50 [f]	22 [h]	*ca.* 2 [i]

[a] Kharasch, Kleiger, and Mayo, *J. Org. Chem.*, 1939, **4**, 430, 433; Kharasch, Norton, and Mayo (*ibid.*, p. 83) record that hydrogen iodide adds to allyl chloride giving exclusively 1-chloro-2-iodopropane. Our results (Part I, *loc. cit.*) suggest, however, that some interaction between the substituent halogen and the developing carbonium ionic centre might occur and divert nucleophilic attack to the 1-position occupied by the neighbouring substituent. One might predict on this basis that a small proportion of 2-chloro-1-iodopropane might be formed, though this might well have escaped detection. [b] Dewael, *Bull. Soc. chim. Belg.*, 1924, **33**, 504. [c] L. Smith and Skyle, *Acta Chem. Scand.*, 1950, **4**, 39, and papers there cited. [d] Part I, *J.*, 1954, . [e] Ingold and H. G. Smith, *J.*, 1931, 2742. [f] Chitwood and Freure, *J. Amer. Chem. Soc.*, 1946, **68**, 680. [g] Boyde and Marle, *J.*, 1908, 839. [h] Ingham and Nichols, *J. Amer. Chem. Soc.*, 1954, **76**, 4472. [i] Winstein and Goodman, *ibid.*, p. 4368.

In the addition reactions, as compared with the oxide ring openings, there is always formed a much greater proportion of the isomer derived by nucleophilic attack at the central (secondary) carbon atom. The present writers take the view that, if the oxide (*B*) and the ion (*C*) undergo ring-opening with nucleophilic attack at the primary carbon atom, as indicated, then there is no reason why the intermediate (*D*) should undergo ring opening in the opposite direction. Dewar (*Discuss. Faraday Soc.*, 1947, **2**, 75; *Bull. Soc. chim.*, 1951, C 71) has realised this point; he suggests that the intermediate in the addition reaction must therefore be a π-complex (*E*). There is, however, clearly no necessity to invoke this hypothesis. It is more reasonable to assume that the intermediate in the addition reaction is an " open " carbonium ion. Stewart and VanderWerf (*J. Amer. Chem. Soc.*, 1954, **76**, 1259) recognise this point, which has also been discussed by de la Mare (in Klyne, " Progress in Stereochemistry," Butterworth, London, in the press). Below, we develop the view that this hypothesis gives a much more ready explanation of the change in orientation with structure and reagent.


(*A*)


(*B*)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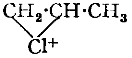
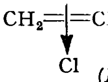

(*D*)

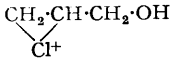

(*E*)

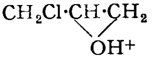
Consideration of Table (*a*) shows, that for propylene and allyl chloride, and presumably also for allyl alcohol, when a proton is the electrophilic reagent leading attack on the molecule, addition is completed entirely by attack at the secondary position. This accords with the *ortho-para*-orienting characteristics of the substituents Me, CH_2Cl, and $CH_2{\cdot}OH$ in aromatic substitutions. It is assumed, therefore, that in the absence of ready interaction between the entering group and the carbonium ionic centre, an electrophilic reagent

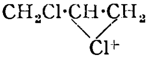
E^+ preferentially and specifically attacks the end carbon atom, to form initially the cation, $E{\cdot}CH_2{\cdot}{}^+CH{\cdot}CH_2X$.

The next point that requires consideration deals with the " neighbouring group " influence of H, Cl, and OH substituents. Winstein *et al.* (*locc. cit.*) have discussed these matters extensively, both for carbonium ions produced in unimolecular solvolyses of halides and alkyl toluene-*p*-sulphonates, and in relation to carbonium ions as intermediates in addition reactions. The hydrogen substituent participates in these reactions only in very special structural situations. The chlorine substituent provides no " driving power " assisting heterolysis. Hence when chlorine is the neighbouring group, the carbonium cation is produced initially and, when the carbonium ionic centre has been formed, interacts with the neighbouring chlorine substituent to allow retention of configuration at the carbonium ionic centre. The hydroxyl substituent contributes a quite substantial driving force assisting heterolysis; hence the interaction of a hydroxyl group with the adjacent carbonium centre must be considerably more favourable energetically than that of a chlorine substituent similarly placed.

The results described in the present paper allow comparison of behaviour of the ions $CH_2Cl{\cdot}{}^+CH{\cdot}CH_2{\cdot}OH$ and $CH_2Cl{\cdot}{}^+CH{\cdot}CH_2Cl$ which, it is presumed, are formed initially in the addition of hypochlorous acid to allyl alcohol and allyl chloride respectively. It is assumed, as has been argued above, that these ions cannot be written in the forms (I*a*), (I*b*), and (II*a*). Furthermore, they do not react by any means completely by transformation into these forms before their reaction with the nucleophilic reagent: for then

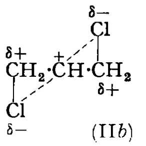

(I*a*)

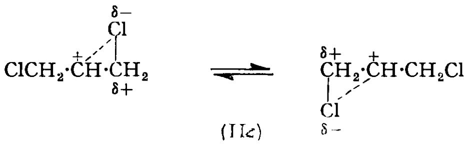

(I*b*)

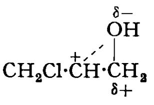

(II*a*)

completion of the attack would involve attack on the primary carbon atom, as, for example, in the acid-catalysed ring opening of epichlorohydrin which is believed to involve (I*b*); whereas, in the addition reactions considered, a substantial part of the reaction gives the product of attack at the secondary position.

The results of the previous paper show also that the intermediate (II) cannot be completely or even largely represented in the form (II*b*) or (II*c*).


(II*b*)

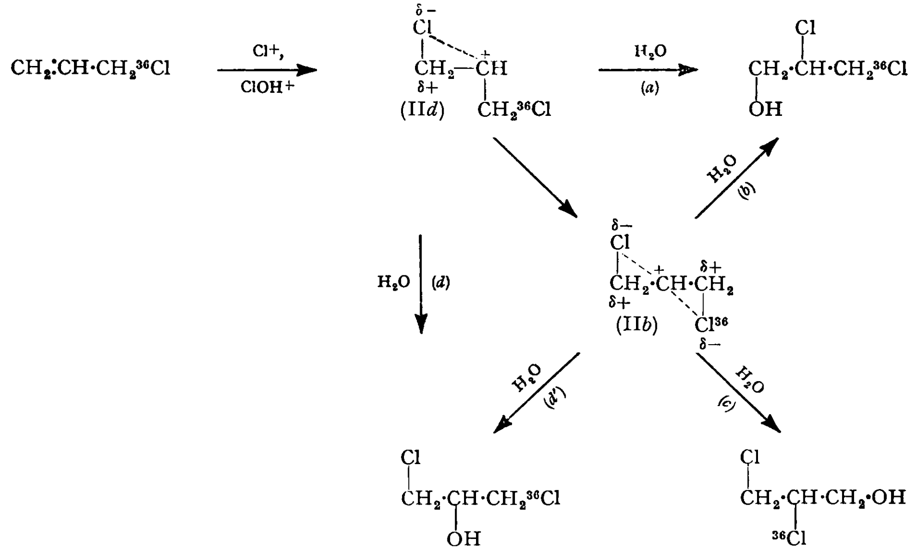

(II*c*)


(I*c*)

Again, it is known from Winstein's work that the hydroxyl group interacts with a carbonium centre considerably more strongly than does a chlorine substituent; so that if the intermediate (I) from allyl alcohol survived long enough for the energetically preferred configuration to be assumed, the form (I*b*) or (I*c*) would be adopted and none of the monochlorohydrin produced in the reaction would have the chlorine substituent in the secondary position. In fact, 25% of the 2-chloropropane-1 : 3-diol is produced.

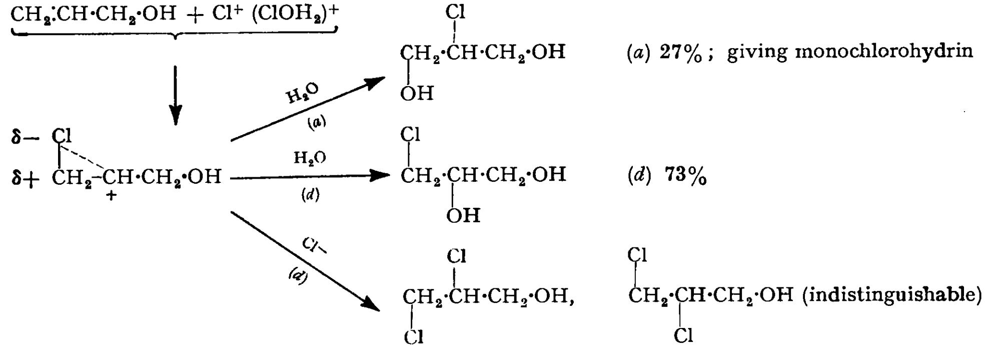
The above considerations restrict to some extent the possibilities which need to be considered in these addition reactions. Below is given a somewhat detailed formulation of the reaction path which may be followed in the addition of hypochlorous acid to allyl chloride.

In the formulation of (II*d*), it is implied that the entering chlorine substituent will in general be situated more favourably, for interaction with the developing carbonium ionic centre, than is the labelled chlorine substituent already present in the molecule. This seems reasonable since, for such interaction to be important, the carbon–halogen bond requires to be displaced to some extent from its usual tetrahedral position. Rotation of the CH_2Cl group would, if the life of the cation were sufficiently long, make the chlorine substituents equivalent; but it seems that reaction (*a*), with the solvent, accompanied by migration of the chlorine from the 1- to the 2-position, may occur so rapidly after the formation of the cation that a substantial part of the reaction follows this path. It is not known whether the migration of the chlorine substituent in this stage is a unimolecular or a bimolecular reaction of the cation; it is possible that the migration is synchronous with attack by the nucleophilic solvent on the 1-position. The transient formation of (II*b*) accounts for at least about 8% of the total reaction; and there is no way of knowing whether a part, if not all, of the reaction following route (*d*) in fact comes from intermediate (II*b*). Some of (II*b*) may also be formed directly from the starting materials, in the case of that fraction of the allyl chloride molecules which were conformationally arranged at the moment of attack so that the two chlorine atoms were situated symmetrically with respect to the central atom.



(*a*) 61%; (*b*) 4%; (*c*) 4%; (*d*) (*d'*) 31%.

The situation for allyl alcohol is rather more simple, since none of the hydroxyl substituent undergoes migration. The reason why the hydroxyl substituent does not migrate, whereas the chlorine substituent does, is probably that the tendency of a hydroxyl substituent to be removed, with its electrons, from a carbon atom is much less than that of a chlorine substituent, as is shown, for example, in the more ready S_N1 and S_N2 displacements of halides compared with alcohols. It is consistent with this view that Smith and Skyle (*loc. cit.*) record that the reaction of hypobromous acid with allyl bromide gives *ca.* 80% of 2 : 3-dibromopropan-1-ol. This suggests that still more migration is possible when the more easily displaced bromine substituent is present. Edwards and Hodges (*J.*, 1954, 761) similarly obtained from the reaction of allyl bromide with bromine acetate some 70%



of 2 : 3-dibromopropyl acetate. This was identified by infra-red measurements, but it is difficult to be certain that the isomer was entirely absent.

The amount of product formed by migration from the point of initial attack increases as the reagent is changed from HCl to ClOH to ICl. We consider this to indicate that migration depends on participation of the entering substituent as a neighbouring group, in the sense in which this term is used by Winstein and his school. In the view developed in this paper, there are two distinct modes of interaction, both of which may result in retention of configuration at the carbonium centre and hence *trans*-addition to olefinic substances. One of these is electrostatic in origin, and is of the type proposed by Cowdrey, Hughes, Ingold, Masterman, and Scott for the α-carboxylate-ion substituent (*J.*, 1937, 1252; cf. also Ingold, *op. cit.*). This type of interaction is available for the chlorine and the hydroxyl substituents, and also probably for the iodine substituent, as is shown in the formation of $CH_2I{\cdot}CHCl{\cdot}CH_3$ in predominant amount from propylene and iodine chloride. The other is, as regards bonding of one of the chlorine substituents, of the " chloronium " type. It might be intermediate between (II*b*) and the product of reaction (*b*) for example, in the above scheme for allyl chloride, provided that this reaction is unimolecular. Experiments relating to other systems and reagents are in progress with a view to testing the general applicability of these views.

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