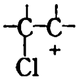
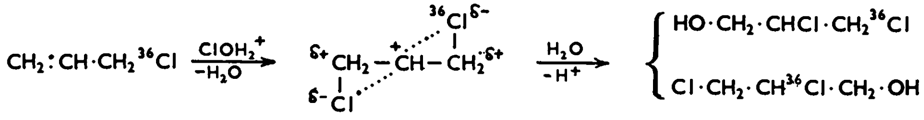
284. *The Kinetics and Mechanisms of Addition to Olefinic Substances. Part IV.* Rearrangement accompanying Addition of Hypochlorous Acid to 3-Chloro-2-methylpropene.*

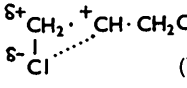
By P. Ballinger and P. B. D. de la Mare.

The addition of hypochlorous acid to 3-chloro-2-methylpropene in water, under catalysis by perchloric acid, gives 1 : 3-dichloro-2-methylpropan-2-ol (94 pts.) and 2 : 3-dichloro-2-methylpropanol (6 pts.). By labelling the 3-chlorine atom in the starting material, and examining the specific activity of 1-chloro-2 : 3-epoxy-2-methylpropane derived from the latter product, it has been shown that 38% of the 2-chlorine atoms in the 2 : 3-dichloro-2-methylpropanol were attached to the 3-carbon atom in the starting material. This result is discussed in terms of the properties of the carbonium ion, which is presumed to be intermediate in the above addition. 2 : 3-Dichloro-2-methylpropanol and αβ-dichloro-α-methylpropionic acid have been characterised for the first time.

Carbonium ions,  $-\underset{Cl}{\underset{|}{C}}-\overset{+}{C}-$, are generally considered to be intermediates in the addition of hypochlorous acid to unsaturated compounds, and stereochemical evidence exists to show that the entering electrophilic chlorine atom can interact, electrostatically or otherwise, with the adjacent carbonium ionic centre. In certain cases, the reactions of such intermediates can be studied by using isotopic tracers. Thus, if hypochlorous acid is added to 3-[^{36}Cl]chloropropene, some of the product is the unsymmetrical dichlorohydrin, 2 : 3-dichloropropanol; and if this is partly or wholly derived from an intermediate symmetrical about the 2-carbon atom, then ^{36}Cl will be found in the 2-position, to an extent which is a measure of reaction by this route.



In fact, study of this addition has shown that only about 12% of the unsymmetrical dichlorohydrin is derived through such a symmetrical intermediate. In principle, the remainder might conceivably have been derived by attack of the electrophilic reagent at the 2-carbon atom to give the carbonium ion, $^+CH_2{\cdot}CHCl{\cdot}CH_2{}^{36}Cl$. It was argued, however, that this was not the main intermediate concerned, since other electrophilic reagents (*e.g.*, HCl, HOH) add to 3-chloropropene to give the product in which the electrophilic part of the addendum (in these cases, H) is attached to the 1-carbon atom. Instead, it was considered that there is produced first the intermediate (I), which then reacts so rapidly with solvent molecules that the chlorine atoms in the carbonium ion do not have time to become completely equivalent.


(I)

If this interpretation is correct, then attachment of electron-releasing groups in the 2-position should stabilise the carbonium ion and allow it to last for a longer time before reaction with the solvent. In this way, reaction through the symmetrical intermediate should be favoured. To test this prediction, the addition has now been examined of hypochlorous acid to 3-chloro-2-methylpropene. In this case, the unsymmetrical chlorohydrin, 2 : 3-dichloro-2-methylpropanol, which must be examined to test the proposed theory, is expected to be formed in relatively small amount, since the 2-methyl group will

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certainly divert the orientation towards the formation of the symmetrical chlorohydrin, 1 : 3-dichloro-2-methylpropan-2-ol. The latter compound is known [1, 2] to be the main product of the addition of chlorine water, or of hypochlorous acid, to 3-chloro-2-methylpropene, and the by-products known in this reaction [2] are those olefinic materials which could be formed by elimination of a proton from the carbonium ion, $CH_2Cl\cdot{}^+CMe\cdot CH_2Cl$, followed by addition to these olefinic substances.

EXPERIMENTAL

Some of the materials and general methods have been described in previous papers.[3] Commercial 3-chloro-2-methylpropene (which contains *ca.* 4% of the isomeric 1-chloro-2-methylpropene, b. p. 69°) was dried and fractionated, the first 10%, which distilled below 72°, being discarded. The major fraction was refractionated with a high reflux ratio and the first 10% being again discarded; the product had b. p. 72·0—72·2°/756 mm., n_D^{25} 1·4250. To label this material with ^{36}Cl, the 3-chloro-2-methylpropene (95 g.) was refluxed for two days with acetone and $Li^{36}Cl$, prepared from $H^{36}Cl$ (3·0 ml. of 1·6N; specific activity 114 μc per g. of Cl; supplied by the Radiochemical Centre, Amersham). The product was washed repeatedly with water to remove acetone and lithium chloride, dried, and fractionated, and had b. p. 72°, n_D^{25} 1·4250.

1 : 3-Dichloro-2-methylpropan-2-ol, prepared from 1 : 3-dichloroacetone and methylmagnesium bromide,[4] had b. p. 63°/12 mm., n_D^{24} 1·4730 (Found: C, 33·5; H, 5·6; Cl, 49·1. Calc. for $C_4H_8OCl_2$: C, 33·6; H, 5·6; Cl, 49·7%). Its reaction with aqueous alkali is very rapid even at 0°, but a rough estimate of the second-order rate coefficient, over the last 5% of the reaction, is k_2 (0·0°) = *ca.* 10^2 l. mole^{-1} min.$^{-1}$.

Preparation of 2 : 3-*Dichloro-2-methylpropanol*.—Methacrylic acid (127 g.) was added slowly to a stirred solution of chlorine in carbon tetrachloride (*ca.* 1 l.) containing a trace of stannic chloride. More chlorine was introduced, and the whole was cooled at *ca.* −80° until the gas ceased to be absorbed. After removal of solvent, the product gave, on fractionation, *αβ-dichloro-α-methylpropionic acid* (160 g.), b. p. 110°/4 mm., n_D^{25} 1·4670, d_4^{25} 1·3629, m. p. 23—24° (Found: C, 30·5; H, 3·9. $C_4H_6O_2Cl_2$ requires C, 30·6; H, 3·8%). Its S-*benzylthiuronium salt* had m. p. 140° (Found: C, 45·2; H, 5·4; N, 8·8; Cl, 22·3; S, 10·0. $C_{12}H_{16}O_2N_2Cl_2S$ requires C, 44·6; H, 5·0; N, 8·7; Cl, 22·0; S, 9·9%). The dichloro-acid (136 g.) was then refluxed for 5 hr. with redistilled thionyl chloride (167 g.). Excess of thionyl chloride was removed, and the product gave on fractionation the acid chloride (98 g.), b. p. 46·5°/11·5 mm., 160°/770 mm., n_D^{25} 1·4670. An ethereal solution of this (98 g.) was added to a stirred suspension of lithium aluminium hydride (18 g.) in ether; then the excess of reagent was decomposed with water, and the ether solution poured into ice and 6N-sulphuric acid. The ether layer was removed, and the aqueous solution was again extracted with ether. The combined ether-extracts were washed with sodium hydrogen carbonate solution, then with water, and dried ($MgSO_4$). Fractionation of the residue gave 2 : 3-*dichloro-2-methylpropanol* (58 g.), b. p. 70°/9 mm., 180°/760 mm. (slight decomp.), n_D^{25} 1·4746, d_4^{25} 1·2680 (Found: C, 33·8; H, 5·7; Cl, 49·6. $C_4H_8OCl_2$ requires C, 33·6; H, 5·6; Cl, 49·7%). The 3 : 5-dinitrobenzoate, prepared in the absence of bases, had m. p. 104°.

Kinetics of the Reaction of 2 : 3-*Dichloro-2-methylpropanol with Aqueous Sodium Hydroxide*.—2 : 3-Dichloro-2-methylpropanol reacts with alkali to give, in good yield, 1-chloro-2 : 3-epoxy-2-methylpropane, as is shown below. It has been presumed that there are no side reactions which significantly affect the measured kinetic form, since titration of a solution containing a known weight of the starting material, after reaction with a known excess of alkali to completion of the reaction of which the kinetic form is measured, gives a result which corresponds, within experimental error, with the release of one mole of hydrogen chloride from one mole of dichlorohydrin. A subsidiary experiment showed that 1-chloro-2 : 3-epoxy-2-methylpropane reacts with alkali under the chosen experimental conditions at a rate which is negligibly slow in comparison with the rate of liberation of the first mole of hydrogen chloride from the dichlorohydrin.

The following is an example of a typical run, in which the chlorohydrin (0·0255M) was allowed to react at 24·9° with 0·0725N-sodium hydroxide. Samples (5·0 ml.) were withdrawn at intervals, quenched in acetone containing 0·0801N-hydrochloric acid (5·46 ml.) and back-titrated with 0·00889N-ethanolic potassium hydroxide, with lacmoid as indicator.

Time (min.)	0·0	0·71	1·49	5·25	8·19	13·51	27·21	∞
Titre (ml.)	8·47	10·20	11·46	16·28	19·00	20·56	22·34	22·88
k_2 (l. mole^{-1} min.$^{-1}$)	—	2·54	2·24	2·31	2·64	2·34	2·25	—

Mean k_2 = 2·39 l. mole^{-1} min.$^{-1}$.

The values for the second-order rate constants are calculated by means of the expression $k_2 = 2{\cdot}303[\log_{10} b(a - x)/a(b - x)]/t(a - b)$, where the symbols have their usual significance. The zero of time is that of mixing of the reactants, and hence the absence of any appreciable rapid initial reaction shows the absence of the fast-reacting 1 : 3-isomer. When the latter is present, a plot of x against time (t) gives a curve, substantially straight near the beginning, which by extrapolation to $t = 0$ gives an estimate of the amount of the faster-reacting isomer in the mixture, since practically all the 1 : 3-isomer has reacted before the first point is taken. Trial determinations by this method with artificial mixtures of the two isomers in known proportion were accurate to ±2 units %.

When equimolecular proportions of the reactants (both 0·0500M) were taken, the mean value of k_2 for pure 2 : 3-dichloro-2-methylpropanol was found to be 2·79 l. mole^{-1} min.$^{-1}$.* Mixtures of the isomers were sometimes assayed in this way, by using the graph of $1/(a - x)$ against t as described previously.[3]

Reaction of Hypochlorous Acid with 3-*Chloro*-2-*methylpropene*.—*Experiment* (i). 3-Chloro-2-methylpropene (71 g.) was dissolved in an aqueous solution (*ca.* 80 l. in a 100 l.-flask) of silver perchlorate (0·02M) and perchloric acid (0·02M), kept at 25° ± 2° by the use of a glass-shielded immersion heater. To the stirred solution was added hypochlorous acid (in total, 3·5 l., 0·166M) 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 mixture was saturated with ether (6 l.), then with sodium chloride (30 kg.). The ether layer was removed and the aqueous solution was extracted with ether (2 × 4 l.). The ether extracts were dried ($MgSO_4$). After removal of the ether, there were obtained fractions : (*a*) 6·2 g., b. p. 27—58°/11 mm., (*b*) 32·5 g. (48%, based on the HOCl taken), b. p. 58·0—60·5°/11 mm., n_D^{25} 1·4725 (Found: C, 33·7; H, 5·7. Calc. for $C_4H_8OCl_2$: C, 33·6; H, 5·6%), (*c*) 3·0 g., b. p. 41—43°/2 mm. The residue from still-pot and column were redistilled, giving (*d*) 1·2 g., b. p. 100—112°/23 mm., and (*e*) tar, 2·9 g. Kinetic analysis showed that fraction (*b*) was nearly pure 1 : 3-dichloro-2-methylpropan-2-ol, whereas fraction (*c*) contained 60% of the latter material and 39% of the isomeric 2 : 3-dichloro-2-methylpropanol. Fractions (*d*) and (*e*) were shown similarly to contain 43% and 34% of the 2 : 3-isomer, together with 34% and 19% of the 1 : 3-isomer respectively, the remainder of each fraction being relatively unreactive with alkali. In order to trace any 2 : 3-isomer in fraction (*b*), 25 g. were dissolved in water (1 l.) and allowed to react for 3 min. at 0° with 2·04N-sodium hydroxide (69 ml., sufficient to hydrolyse 80% of the dichloro-2-methylpropanol). The mixture was extracted with ether and the extract was dried ($MgSO_4$) and fractionated. After removal of ether and 1-chloro-2 : 3-epoxy-2-methylpropane, there were recovered 4·0 g. of the expected 5·0 g. of undecomposed dichloro-2-methylpropanol, b. p. 51·5°/9 mm., n_D^{25} 1·4720. Kinetic analysis revealed the presence of *ca.* 18% of 2 : 3-dichloro-2-methylpropanol; fraction (*b*) thus contained *ca.* 3% of the latter substance. From these determinations, it was possible to assign an approximate value (6—7%) to the proportion of 2 : 3-dichloro-2-methylpropanol recovered from the reaction between hypochlorous acid and 3-chloro-2-methylpropene.

Experiment (ii). 3-[^{36}Cl]Chloro-2-methylpropene (40 ml.) was added in 5 ml. portions to a stirred aqueous solution (*ca.* 8 l. in a blackened vessel) of silver perchlorate (0·02M) and perchloric acid (0·02M), in a thermostat at 24·9°. To this was added 0·211M-hypochlorous acid (in total, 1·92 l.) at such a rate that the concentration of hypochlorous acid in the reaction mixture never exceeded 0·001M. Further measured quantities of silver perchlorate and perchloric acid were added at intervals to keep their concentration at the initial value. On

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* The difference between this value and that recorded above probably should be associated with the variation in second-order rate coefficients with concentration of alkali, attributed [5] to the formation, in bulk, of the intermediate alkoxide.

[1] Suter and Malkemus, *J. Amer. Chem. Soc.*, 1941, **63**, 980; Hurd and Abernethy, *ibid.*, p. 976.

[2] Burgin, Hearne, and Rust, *Ind. Eng. Chem.*, 1941, **33**, 386.

[3] de la Mare and Pritchard, *J.*, 1954, 3910, 3990.

[4] Gibson, Harley-Mason, Litherland, and Mann, *J.*, 1942, 171.

[5] Twigg, Wise, Lichtenstein, and Philpotts, *Trans. Faraday Soc.*, 1952, **48**, 699.

completion of the reaction, the mixture was saturated with ether, then with anhydrous sodium sulphate. The ether layer was removed, the aqueous portion was extracted with ether (3 × 1·3 l.), and the ether extracts were dried ($MgSO_4$) and fractionated. After removal of the ether, the crude material was evaporated at 3 mm. pressure into a series of three traps, cooled in ice, carbon dioxide–ethanol, and liquid nitrogen, respectively. The liquid in the ice-trap (40·1 g., 69% based on the hypochlorous acid taken) proved on fractionation to be almost exclusively a mixture of the isomeric dichlorohydrins produced in the reaction. To this was added pure inactive 2 : 3-dichloro-2-methylpropanol (8·377 g.), and the mixture was fractionated. The following fractions were obtained: (*a*) 2·7 g., b. p. 49—52°/8 mm., n_D^{25} 1·4705, (*b*) 28·1 g., b. p. 52·3—52·5°/8 mm., n_D^{25} 1·4724, (*c*) 7·2 g., b. p. 52·5—64·5°/8 mm., and (*d*) 8·45 g., b. p. 64·5—65·0°/8 mm., n_D^{25} 1·4745.

Kinetic analysis of these fractions showed that fraction (*a*) contained 82% of 1 : 3-dichloro-2-methylpropan-2-ol (instantaneous reaction with alkali), with 18% of a substance having k_2 = *ca.* 47 l. mole^{-1} min.$^{-1}$; fraction (*b*) was nearly pure 1 : 3-dichloro-2-methylpropan-2-ol (Found: C, 33·3; H, 5·6%); fraction (*c*) contained 29·1% of 2 : 3-dichloro-2-methylpropanol (k_2 = 2·74 l. mole^{-1} min.$^{-1}$); and fraction (*d*) contained 97% of the latter isomer, k_2 = 2·73 l. mole^{-1} min.$^{-1}$.

A sample of the original 3-chloro-2-methylpropene was hydrolysed with aqueous sodium hydroxide at 60°. The solution was just acidified (sulphuric acid), evaporated to dryness, and ignited. The products were dissolved in water, the solution was filtered, and the total chloride determined (Volhard). Known weights of the other samples were dissolved in water, and their radioactivities determined by the technique usual for liquid samples. The results of radioactive measurements on these samples are shown in Table 1. From these the specific activity of the pure diluted 2 : 3-dichloro-2-methylpropanol is estimated as 1020. From this, and the weight : dilution ratio of the chlorohydrin mixture obtained from the reaction (40·1 g. of chlorohydrin mixture with 8·377 g. of inactive 2 : 3-dichloro-2-methylpropanol), it is estimated that the percentage of 2 : 3-dichloro-2-methylpropanol in the mixture obtained from the addition reaction was 6·0%, in good agreement with the result of experiment (i).

TABLE 1. *Radioactive measurements on samples from the reaction of hypochlorous acid with labelled 3-chloro-2-methylpropene.*

Sample	Composition	Concn. (M)	Counts/ min.[a]	Spec. activity[b]
1	NaCl from $^{36}Cl{\cdot}CH_2{\cdot}CMe{:}CH_2$	0·05357	244·5	4562 ± 40
2	1 : 3-Dichloro-2-methylpropan-2-ol [fraction (*b*)]	0·1010	458·4	4538 ± 30
3	Mixed dichlorohydrins [fraction (*c*); 29·1% of 2 : 3-dichloro-2-methylpropanol]	0·1015	357·8	3537 ± 18
4	2 : 3-Dichloro-2-methylpropanol, 96·9% [fraction (*d*)]	0·1017	115·3	1137 ± 10

[a] Counts are corrected for background (*ca.* 10/min.). [b] Specific activity is defined here arbitrarily as counts per min. calc. for a M-solution for a particular G.M. tube used for all the measurements. The probable errors are calculated on the basis of random fluctuations in the rate of counting.

Fraction (*d*) (6·904 g.) was diluted with pure inactive specimens of 2 : 3-dichloro-2-methylpropanol (9·344 g.) and 1 : 3-dichloro-2-methylpropan-2-ol (1·895 g.) and refractionated; 12·2 g., b. p. 65—67°/9 mm., were collected. Kinetic analysis showed the continued presence of the diluted 1 : 3-isomer, and this was removed as follows. The mixture (11·3 g.) was hydrolysed in water (150 ml.) at 27° for 2 min. with 0·1N-sodium hydroxide (80 ml., sufficient to destroy 10% of the mixture). It was then extracted with ether, and the ether extract was dried and fractionated. After removal of the ether a fraction (7·7 g.) having b. p. 57°/7 mm. was obtained. Kinetic analysis then revealed, within the experimental error (*ca.* 0·5 unit %), no 1 : 3-dichloro-2-methylpropan-2-ol.

This material was diluted again with pure inactive material to give a sample of pure 2 : 3-dichloro-2-methylpropanol (specific activity, 160·3). The mixture (18·1 g.), in water (600 ml.), was hydrolysed completely to the epoxide with 1·58N-sodium hydroxide (81 ml.) at 27° for 30 min., then saturated with ether, and the ether was salted out with anhydrous sodium sulphate. The aqueous layer was kept for counting (sample 8), and the ether extracts were dried and fractionated. There were obtained 10·1 g. (80% yield), b. p. 121·5—122·5°, together with small quantities of unchanged 2 : 3-dichloro-2-methylpropanol (1·1 g.), b. p. 61°/8 mm., and material of higher b. p. (*ca.* 0·5 g.). Refractionation gave pure 1-chloro-2 : 3-epoxy-2-methylpropane (4·2 g.), b. p. 122·5°/766 mm., n_D^{25} 1·4308 (cf. ref. 6) (Found : C, 45·1; H, 6·7. Calc. for C_4H_7OCl : C, 45·1; H, 6·6%).

Known weights of the diluted 2 : 3-dichloro-2-methylpropanol and of the derived epoxide were dissolved in ethanol, and their specific activities were determined. As an additional check, these two samples, after counting, were hydrolysed completely by refluxing with excess of 4·5N-sodium hydroxide for 8 hr. The products were just acidified with sulphuric acid, evaporated to dryness, and fused in a silica crucible.

The aqueous layer from the bulk hydrolysis of 2 : 3-dichloro-2-methylpropanol was just acidified with sulphuric acid, and the volatile material was evaporated under a high vacuum. The residue was ignited. Each of the three ignited samples was dissolved in water and filtered. The specific activities of these samples were measured (see Table 2).

TABLE 2. *Radioactive measurements on 2 : 3-dichloro-2-methylpropanol and 1-chloro-2 : 3-epoxy-2-methylpropane.*

Sample	Material	Solvent	Concn.	Count/ min.[a]	Spec. activity[b]
1	2 : 3-Dichloro-2-methylpropanol	EtOH	1·901	304·9	160·3 ± 1·3
2	1-Chloro-2 : 3-epoxy-2-methylpropane from sample 1	EtOH	2·857	371·2	129·9 ± 1·0
3	Total chloride from sample 1	H_2O[c]	1·752	113·3	129·4[d] ± 1·7
4	Total chloride from sample 2	H_2O	1·802	189·3	105·1 ± 1·2
5	Chloride from partial hydrolysis of sample 1 ...	H_2O	0·953	28·1	29·5 ± 0·5

[a, b] See footnotes to Table 1. [c] Solutions of compounds containing ^{36}Cl in ethanol and water give counts differing approximately in the ratio 1·24 : 1. [d] After correction for the fact that 2 : 3-dichloro-2-methylpropanol (1 mole) gives sodium chloride (2 moles).

Experiment (iii). Radioactive 3-chloro-2-methylpropene (12 ml.) was added to a stirred solution (9 l.) of silver perchlorate (0·02M) and perchloric acid (0·02M) in a blackened vessel at 25°. 0·131M-Hypochlorous acid (8 × 50 ml.) was added during 3½ hr. Pure inactive 1 : 3-dichloro-2-methylpropan-2-ol (6·136 g.) was then added and the solution was extracted with pentane (500 g.). The pentane extract was dried and fractionated. There were recovered 1·7 g. of 3-chloro-2-methylpropene, b. p. 70—72°/760 mm., still slightly contaminated with pentane but completely free from other products. Samples of this, and of the original 3-chloro-2-methylpropene, were hydrolysed with sodium hydroxide in 50% ethanol. The solutions were just acidified with sulphuric acid, evaporated to dryness, and dissolved in water. The specific activities were found to be respectively 1933 ± 16 and 1911 ± 17, identical within statistical error.

The aqueous residue from the addition reaction, after extraction with pentane, was saturated with ether and then with sodium sulphate. The ether layer was removed and the aqueous solution was again extracted with ether (in all, 3½ l.). The ether solutions were combined, dried ($MgSO_4$), and fractionated. After removal of the ether, there was recovered 1 : 3-dichloro-2-methylpropan-2-ol, b. p. 60°/11 mm., n_D^{25} 1·4718, specific activity 879 ± 8. From the degree of dilution of the formed 1 : 3-dichloro-2-methylpropan-2-ol, the specific activity of which must be the same, on a molar basis, as that of the original 3-chloro-2-methylpropene, it can be calculated that from 0·0524 mole of hypochlorous acid there was produced 0·03655 mole (70%) of 1 : 3-dichloro-2-methylpropan-2-ol.

Subsidiary Experiment.—To show that exchange of ^{36}Cl between the two chlorohydrins during the working up of the reaction mixture is unimportant, the following experiment was performed. Labelled 1 : 3-dichloro-2-methylpropan-2-ol (specific activity, 21,470; 0·682 g.) was mixed with inactive 2 : 3-dichloro-2-methylpropanol (5·549 g.). The mixture (overall specific activity, 2374) was hydrolysed at 20° for 2 min. with enough alkali to decompose 10% of the dichlorohydrin. The residue was recovered and fractionated, early fractions being discarded and unchanged 2 : 3-isomer collected. After removal, by further alkaline hydrolysis, of the remaining contaminating 1 : 3-dichloro-2-methylpropan-2-ol, the residual material gave, on alkaline hydrolysis, chloride of specific activity 32. Thus the above procedure contaminates negligibly (*ca.* 1%, under the conditions of the above experiment) the 2-carbon atom of 2 : 3-dichloro-2-methylpropanol.

DISCUSSION

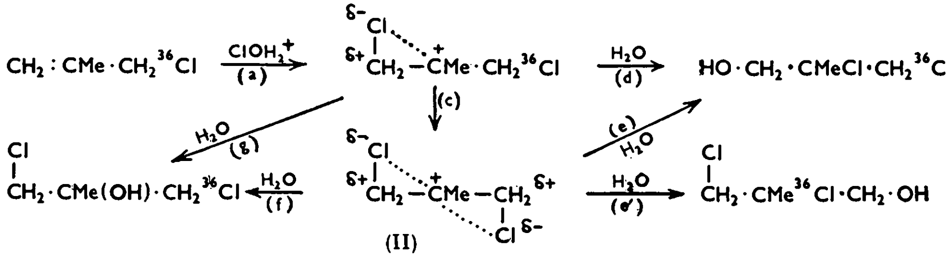
Formation of 2 : 3-*Dichloro-2-methylpropanol from Hypochlorous Acid and* 3-*Chloro-2-methylpropene.*—2 : 3-Dichloro-2-methylpropanol does not seem to have been characterised previously, though its dibromo-analogue has been prepared.[7] In the present work, it has been shown that it can be separated from its isomer, 1 : 3-dichloro-2-methylpropan-2-ol, by fractionation, and that it can be characterised and distinguished by its much slower rate of reaction with hydroxide ions in water. In these respects, it resembles its lower homologue.

Addition of hypochlorous acid, under catalysis by perchloric acid, to 3-chloro-2-methylpropene gives, as main product, 1 : 3-dichloro-2-methylpropan-2-ol. Under preparative conditions for addition of hypochlorous acid, this is well established from the work of other investigators. Kinetic analysis of the later chlorohydrin fractions from this reaction shows clearly, however, that 2 : 3-dichloro-2-methylpropanol is a minor product, amounting to about 6% of the total chlorohydrin produced. Addition to 3-chloropropene gives 70% of the analogous chlorohydrin,[3] so the presence of the 2-methyl substituent has modified the orientation considerably, in the direction that would be expected in view of the electron-donating capacity of this group.

Rearrangement accompanying Addition of Hypochlorous Acid to 3-*Chloro-2-methylpropene.*—In a previous paper,[3] it was argued that, in the absence of significant interaction between the entering electrophilic group, E, from the reagent EX, and the carbonium ionic centre, the orientation in addition to 3-chloropropene would be substantially the product of attachment of E to the 1-carbon atom. Still more should this be the case in the present example, and this can be supported by the experimental evidence that addition to this olefinic substance of hydrogen chloride gives 1 : 2-dichloro-2-methylpropane,[8] and addition of water gives 1-chloro-2-methylpropan-2-ol.[2]

The small amount of 2 : 3-dichloro-2-methylpropanol formed in the reactions described herein results, on the view proposed, from intermediates and by routes such as are indicated in the scheme below [sequences (a), (d), and (a), (c), (e) or (e′)].

Proposed sequence for reaction of hypochlorous acid with 3-*chloro-2-methylpropene.*



Two extreme results might be sought on this hypothesis. If reaction (d) occurred before the carbonium ion had time to acquire symmetry in reaction (c), then the 2-chlorine atom in the product would be derived entirely from the hypochlorous acid. If, on the other hand, the carbonium ion lasted long enough in solution to enable the 3-chlorine atom to become equivalent with the 1-chlorine atom, then any chlorine atoms ending up on the 2-position should, by way of such an intermediate as (II), have specific activity which was half that of the original 3-chloro-2-methylpropene.

In the present set of experiments, following the lines of the previous investigation, the specific activity has been examined of the 3-chlorine atom by converting the 2 : 3-dichloro-2-methylpropanol by alkaline hydrolysis into 1-chloro-2 : 3-epoxy-2-methylpropane,

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[6] Hearne and De Jong, *Ind. Eng. Chem.*, 1941, **33**, 940; Pritchard and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 2667.

[7] Pogorshelski, *J. Russ. Phys. Chem. Soc.*, 1904. **36**, 1129.

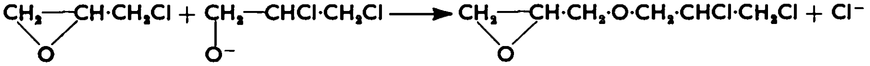
[8] Burgin, Engs, Groll, and Hearne, *Ind. Eng. Chem.*, 1939, **31**, 1413.

and examining the specific activity of this material. The results, shown in the Tables, indicate that a sample of labelled 3-chloro-2-methylpropene of specific activity 4562 gave a combined dichlorohydrin fraction of specific activity 4538, unchanged within experimental error; and this, after dilution, gave 2 : 3-dichloro-2-methylpropanol of specific activity 160·3, from which was obtained 1-chloro-2 : 3-epoxy-2-methylpropane of specific activity 129·9. If the original addition of hypochlorous acid had proceeded entirely through a completely symmetrical intermediate (*e.g.*, II), then the specific activity of the recovered epoxide would have been 160·3/2 = 80·15. Hence the proportion of reaction proceeding through such an intermediate is (160·3—129·9)/(160·3—80·15) = 30·4/80·15 = 0·38; *i.e.*, 38%. The remainder must come by way of an unsymmetrical intermediate, *e.g.*, through reaction (d) of the scheme.

Previously[3] it was shown that the corresponding result for the reaction of 3-chloropropene with hypochlorous acid was 12%. The increased degree of rearrangement accompanying the addition to 3-chloro-2-methylpropene is in accordance with, and in the authors' view, supports the proposed mechanism. The 2-methyl substituent, being attached to the carbonium ionic centre in the intermediate, stabilises this and therefore this intermediate has a greater life in solution. As a consequence, the two chlorine substituents have more opportunity to become equivalent. It is noteworthy, however, that even in this tertiary carbonium ion, complete equivalence of the chlorine atoms is not achieved before reaction is completed by entry of the hydroxyl group.

It has been confirmed (experiment iii) that the first stage (a) of the addition reaction is not appreciably reversible, since, if it were, appreciable dilution of the 3-chloro-2-methylpropene would occur during the reaction by loss of the 3-chlorine atom, which can become, in part, structurally equivalent to the entering chlorine. In fact, excess of 3-chloro-2-methylpropene could be recovered unchanged in specific activity after the reaction. This experiment shows also that there is no adventitious dilution of the starting material during the reaction or in the working up.

Intermolecular Condensation during the Hydrolysis of 2 : 3-*Dichloro-2-methylpropanol*.—If the inorganic chloride derived from the 2 : 3-dichloro-2-methylpropanol under conditions of mild alkaline hydrolysis were representative of the chlorine from the 2-carbon atom, then the specific activity of this chloride would have been a direct measure of the extent of rearrangement. The value obtained by using the specific activity of sample 5 (see Table 2) is 45%, significantly higher than that derived from the measurement of the specific activity of the 1-chloro-2 : 3-epoxy-2-methylpropane. A similar, but greater discrepancy, was experienced in the earlier study[3,9] of the lower homologous system. In that case, the source of error was shown to be a side reaction, the cross-condensation, under conditions of mild alkaline hydrolysis, with bimolecular displacement at the terminal carbon atom, by such a reaction as the following:



$$\underset{O}{CH_2\text{—}CH}\cdot CH_2Cl + \underset{O^-}{CH_2}\text{—}CHCl\cdot CH_2Cl \longrightarrow \underset{O}{CH_2\text{—}CH}\cdot CH_2\cdot O\cdot CH_2\cdot CHCl\cdot CH_2Cl + Cl^-$$

In the present case, such side reactions are theoretically much less likely, for not only are the chlorohydrins themselves much more reactive in the competing internal nucleophilic displacements, but also the 2-methyl group must introduce steric hindrance[10] to displacement either at the 3- or at the 2-carbon atom. This theoretical justification is supported experimentally by the fact that the intramolecular condensation, to form 1-chloro-2 : 3-epoxy-2-methylpropane, of 1 : 2-dichloro-2-methylpropanol is accompanied by definite, but relatively small amounts of high-boiling material detectable by fractionation.

Elimination accompanying the Addition.—The dichlorohydrin mixture produced in the reaction accounts, as shown in experiment (iii), for 75% of the amount of hypochlorous acid used up in the reaction between this and excess of 3-chloro-2-methylpropene. The

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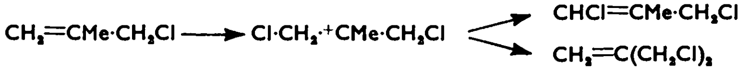
[9] de la Mare and Pritchard, *J.*, 1954, 1644.

[10] Dostrovsky, Hughes, and Ingold, *J.*, 1948, 1283.

remaining products of the reaction presumably result from elimination from the carbonium ion :



$$CH_2{=}CMe{\cdot}CH_2Cl \longrightarrow Cl{\cdot}CH_2{\cdot}{}^{+}CMe{\cdot}CH_2Cl \begin{array}{l} \nearrow CHCl{=}CMe{\cdot}CH_2Cl \\ \searrow CH_2{=}C(CH_2Cl)_2 \end{array}$$

Other possibilities exist if hydrogen or chlorine migrates to the 2-position in the carbonium ion before elimination occurs. In Burgin, Hearne, and Rust's experiments,[2] such products might also have reacted, with chlorine, to give the tri- and tetra-chlorinated products which they isolated. Investigation of this aspect of the problem awaits further studies of the products of elimination from carbonium ions.[11]

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