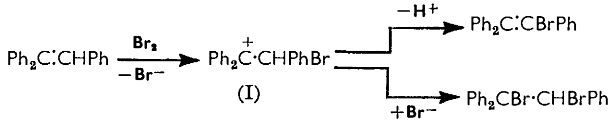
498. *The Kinetics and Mechanisms of Additions to Olefinic Substances. Part VI.*[1] *Olefin-forming Proton-loss accompanying Addition of Hypochlorous Acid to 2,3-Dichloropropene.*

By P. Ballinger, P. B. D. de la Mare, and D. L. H. Williams.

By using the method of isotopic dilution, it has been shown that addition of hypochlorous acid to 2,3-dichloropropene is accompanied by substitution, which gives 3·7% of *cis*- and 4·3% of *trans*-1,2,3-trichloropropene, based on the consumption of hypochlorous acid. By starting with 2,3-dichloropropene allylically labelled with ^{36}Cl and examining the ratio of allylic to vinylic labelling in the product, it has been shown that only 22% of the *cis*-olefinic product, and only 11% of the *trans*-olefinic product is derived by proton-loss from the attacked carbon atom. The unchanged 2,3-dichloropropene, as well as the isolated products, including *sym.*-dichloroacetone, have the same specific activity as the reactant olefin. The chloride ion liberated in the reaction is derived in part from the reacting hypochlorous acid and in part from the 2-, but to a negligible extent from the 3-chlorine atom of the 2,3-dichloropropene. These results provide further information concerning the reactions of the carbonium ion formed from hypochlorous acid and 2,3-dichloropropene, and the stereochemical factors concerned in determining the direction of proton-loss from halogen-substituted carbonium ions.

Of recent years it has become apparent that carbonium ions often undergo reactions which reflect the dynamic stereochemistry of their formation. Examples from several fields have been referred to elsewhere,[1,2] and earlier parts of the present series have been concerned, *inter alia*, with this principle as applied to the addition of hypohalous acids to olefins.[3,4]

Electrophilic substitution at olefinic centres is of interest in this connection. Reactions of this type are well known, and are very characteristic of di- and poly-aryl-substituted olefins. Thus triphenylethylene with bromine can, according to the conditions, give mainly either the product of substitution, bromotriphenylethylene, or of addition, 1,2-dibromo-1,2,2-triphenylethane:[5]



$$Ph_2C{:}CHPh \xrightarrow[-Br^-]{Br_2} Ph_2\overset{+}{C}{\cdot}CHPhBr \;(I) \xrightarrow{-H^+} Ph_2C{:}CBrPh$$

$$Ph_2\overset{+}{C}{\cdot}CHPhBr \;(I) \xrightarrow[+Br^-]{} Ph_2CBr{\cdot}CHBrPh$$

Such a reaction would generally be held [cf. 6] to proceed through a substituted carbonium ion [*e.g.*, (I)]. In many other cases, the proton-loss which follows electrophilic attack may give isomeric olefinic products, so that the overall reaction in part appears to be a substitution at a saturated carbon atom, though in fact it is a substitution accompanied by rearrangement of the double-bond system.[7] Thus the main product of chlorination of isobutene under aprotic conditions is 3-chloro-2-methylpropene (II),[cf. 6] which is also the main olefinic product obtained from isobutene and hypochlorous acid in water.[8]

It having been recognised that such reactions often involve halogen-substituted carbonium ions, a theory concerning the orientation of proton-loss in such cases was developed[6]

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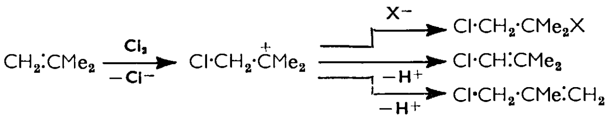
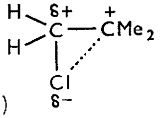
[1] Part V, de la Mare and Galandauer, *J.*, 1958, 36.
[2] de la Mare, *Ann. Reports*, 1957, **54**, 160.
[3] de la Mare and Pritchard, *J.*, 1954, 3910, 3990.
[4] Ballinger and de la Mare, *J.*, 1957, 1481.
[5] Meisenheimer, *Annalen*, 1927, **456**, 139.
[6] Taft, *J. Amer. Chem. Soc.*, 1948, **70**, 3364.
[7] Reeve, Chambers, and Prickett, *J. Amer. Chem. Soc.*, 1952, **74**, 5369.
[8] de la Mare and Salama, *J.*, 1956, 3337.

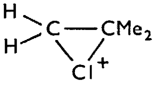


(II)

in terms of the polar effects of the substituents attached to the carbonium ionic centre. An alternative theory was put forward, and was considered to be preferable, by de la Mare and Salama,[8] who associated proton-loss to form predominantly the allylic halide (II) with distortion of the chloromethyl group towards a three-membered ring by interaction between the C–C dipole and the carbonium ionic centre, as might be formulated by either structure (III) or (IV). It was considered that this would stereochemically be unfavourable for proton-loss, and would therefore allow this process to occur predominantly in the methyl groups.*

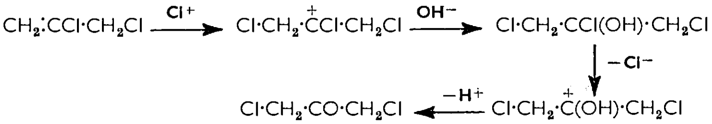


(III)



(IV)

Further test of this hypothesis becomes possible in symmetrical systems, in which the direction of proton-loss can be defined by tracer studies. One such system is that in which hypochlorous acid reacts, under the influence of acids as catalysts, with 2,3-dichloropropene. Additions of hydrogen chloride and of hydrogen fluoride to this compound [9,10] give the product expected if electrophilic attack by the proton is initiated at the 1-carbon atom. Chlorination in water was shown by Henry [11] to give, in about 50% yield, *sym.*-dichloroacetone, presumably by the following sequence:



The other possible product of addition of hypochlorous acid, 2,2,3-trichloropropan-1-ol, has never been described; the products of substitution, *cis*- and *trans*-1,2,3-trichloropropene, had not been isolated from the present reaction before this investigation, but they have been characterised, and their configurations have been established.[12]

In a preliminary communication,[13] it was recorded that 1,2,3-trichloropropene could be obtained from 2,3-dichloropropene and hypochlorous acid in water, with perchloric acid as catalyst, and silver perchlorate to prevent the formation of free chlorine. The present paper confirms and amplifies this report and describes some of the stereochemical features of this reaction, as well as some characteristics of that part of the reaction which gives *sym.*-dichloroacetone.

EXPERIMENTAL

Most of the general methods have been described in previous papers in this series. Infrared spectra were determined with a Grubb-Parsons spectrophotometer. Separations by vapour-phase chromatography were made with a commercial apparatus, with kieselguhr as the support for the liquid phase of dinonyl phthalate, the temperature being *ca.* 90° and nitrogen being the carrier gas. We are indebted to Mr. D. G. Hare for assistance with these separations.

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* Arguments that structures like (III) are more important than those like (IV) for chlorine-substituted (though perhaps not for bromine-substituted) carbonium ions have already been adduced.[3,4]

[9] Friedel and Silva, *Jahresber. Fortschr. Chem.*, 1871, 404; 1872, 322.

[10] Henne and Haeckl, *J. Amer. Chem. Soc.*, 1941, **63**, 2692.

[11] Henry, *Compt. rend.*, 1882, **94**, 1428.

[12] Hatch, D'Amico, and Ruhnke, *J. Amer. Chem. Soc.*, 1952, **74**, 123.

[13] Ballinger and de la Mare, *Chem. and Ind.*, 1957, 1545.

2,3-Dichloropropene was purified by fractional distillation; it had b. p. 93·4°/760 mm., n_D^{25} 1·4578. [3-^{36}Cl]-2,3-Dichloropropene was prepared from this by refluxing it with acetone and lithium chloride-36. The product was washed with water, dried, and fractionally distilled; it had b. p. 94·0°/771 mm., n_D^{25} 1·4574.

2-*Chloroallylthiouronium picrate* was prepared by refluxing either of the above materials with thiourea in methylated spirit,[14] followed by addition of picric acid. The product was precipitated by adding a little water, and was recrystallised; it had m. p. 172° (Found: C, 31·9; H, 3·0; Cl, 9·3; N, 18·6; S, 8·1. $C_{10}H_{10}O_7ClN_5S$ requires C, 31·6; H, 2·7; Cl, 9·3; N, 18·5; S, 8·4%). This material, when prepared from [3-^{36}Cl]-2,3-dichloropropene prepared as described above, had no radioactivity; so, as was expected, the 2,3-dichloropropene was labelled specifically in the 3-position. The isomeric trichloropropenes were prepared by the route:[12] $CH_2{:}CCl{\cdot}CH_2Cl \xrightarrow{Cl_2} ClCH_2{\cdot}CCl_2{\cdot}CH_2Cl \xrightarrow[-HCl]{KOH} CHCl{:}CCl{\cdot}CH_2Cl$. The products were separated by careful fractional distillation, and had the following properties: *cis*-isomer, b. p. 87°/100 mm., n_D^{25} 1·5020; *trans*-isomer, b. p. 75°/100 mm., n_D^{25} 1·4957. Their infrared spectra accorded with those reported by Hatch, D'Amico, and Ruhnke,[12] and characterised both isomers as at least 99% pure. Vapour-phase chromatography showed that each gave a single peak, and appeared to be uncontaminated with any trace of impurity. Mixtures of the two gave completely separated peaks in which the *trans*- ran ahead of the *cis*-isomer.

A mixture of these isomers was labelled in the 3-position as described for [3-^{36}Cl]-2,3-dichloropropene. The product was fractionated, and the individual isomers were converted into their thiouronium picrates. These had no radioactivity and had the following properties: cis-1,2-*dichloroallylthiouronium picrate*, m. p. 153° (Found: C, 29·4; H, 2·6; Cl, 17·5; N, 17·4; S, 7·8. $C_{10}H_9O_7Cl_2N_5S$ requires C, 29·0; H, 2·2; Cl, 17·2; N, 16·9; S, 7·7%); trans-1,2-*dichloroallylthiouronium picrate*, m. p. 184° (Found: C, 29·7; H, 2·1; Cl, 17·7; N, 16·8; S, 8·1%).

Radioactively labelled *cis*-1,2,3-trichloropropene was mixed with the inactive *trans*-isomer and fractionally distilled; the recovered *trans*-compound was inactive. Similarly, when labelled *trans*-1,2,3-trichloropropene was mixed with the inactive *cis*-isomer and fractionally distilled, the latter material was recovered and was shown to be completely inactive. So no exchange occurs between the isomers during fractionation.

The following methods were used for assaying the specific activities of the polychloro-compounds. For some samples, the activities were determined directly in solution in ethanol. For others, the compound was decomposed completely by heating it with magnesium, essentially as described by Fedoseev and Ivashova.[15] The product was dissolved in water, and the radioactivity and chloride content were determined in the usual way. The specific activity was calculated on the assumption that by this method all the chlorine in the compound had been liberated as chloride. In still other cases, 2,3-dichloropropene or 1,2,3-trichloropropene was partially hydrolysed by heating it under reflux with 1 equiv. of lithium ethoxide in aqueous ethanol. The volatile material was then removed as completely as possible under reduced pressure; the residue was dissolved in water and extracted with ether to remove the last trace of organic material; and the aqueous solution was then evaporated, and the residue taken up in ethanol, to give a solution used for determination of radioactivity and chloride ion. It was shown, by comparison with the radioactivity of samples of the compounds specifically labelled in the allylic position on which the radioactivity had been determined directly, that hydrolysis under these conditions removes only the allylic chlorine atom. Appropriate correction[3] was made when it was necessary to compare radioactivity determined in ethanol and in water.

Reaction of Hypochlorous Acid with 2,3-*Dichloropropene*.—(1) [3-^{36}Cl]-2,3-Dichloropropene (49·4 g.) was added to a stirred solution (*ca.* 20 l.) of silver perchlorate (0·05M) and perchloric acid (0·5M) at 24° in a blackened vessel. Hypochlorous acid (1814 ml., 0·315 mole) was added in 100 ml. portions at intervals during 2 hr. The reaction was allowed to continue for 24 hr., by which time all the hypochlorous acid had been used up. The solution was filtered, and the precipitate was washed with acetone, dried, dissolved with ammonia, and reprecipitated. The precipitate was weighed (64·8 g., 0·45 mole); a portion was converted into hydrogen chloride by reduction, and a solution of this was examined for chloride content and radioactivity. The filtrate from the reaction was extracted with pentane, and the extract was dried and fractionally distilled. After removal of the pentane, two fractions were obtained; (*a*) 2·7 g., b. p.

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[14] Levy and Campbell, *J.*, 1939, 1443.

[15] Fedoseev and Ivashova, *Zhur. analit. Khim.*, 1956, **11**, 233; *Chem. Abs.*, 1956, **50**, 14,446.

94·0°/765 mm., n_D^{25} 1·4562; (*b*) 3·0 g., b. p. 94·0—94·5°/765 mm., n_D^{25} 1·4571. These were nearly pure unchanged 2,3-dichloropropene. The residues in the still-pot were transferred to a small fractionating column and fractionated; there were recovered 3 g., b. p. 143—144°/760 mm., which on refractionation gave two fractions: (*c*) 1 g., b. p. 130—143°/760 mm., n_D^{25} 1·4906; (*d*) 1 g., b. p. 143—148°/760 mm., n_D^{25} 1·4978. This was a mixture of *cis*- and *trans*-1,2,3-trichloropropene, as was confirmed by examination of its infrared spectrum.

The aqueous layer remaining after extraction with pentane was saturated with ether and salted out with sodium sulphate. The ether layer was removed, and the solution extracted twice more with ether. The combined extracts were washed with water, dried, and fractionally distilled. After removal of the ether, there were obtained the following fractions: (*e*) 0·9 g., b. p., 38—40°/10 mm.; (*f*) 0·8 g., b. p. 61·5—62°/10 mm., n_D^{25} 1·4728; (*g*) 0·8 g., b. p. 62·5°/10 mm., n_D^{25} 1·4755; (*h*) 0·7 g., b. p. 62·5°/10 mm., n_D^{25} 1·4798 [fractions (*g*) and (*h*) solidified on being kept]; (*i*) 5·3 g., b. p. 62·8—63·2°/10 mm., solidifying in the collecting tube; (*k*) 1·7 g., b. p. 76—78°/6 mm. Towards the end of the distillation, flashes of light were seen in the column, and a mass of friable material remained as residue. Fraction (*i*) was recrystallised to constant specific activity and constant m. p. 42° from light petroleum.

The specific activities of the original 2,3-dichloropropene, and of fractions (*b*), (*d*), and (*i*) were determined. Fraction (*i*) was then partially hydrolysed with 1·2 ml. of 0·5N-sodium hydroxide for 20 hr. at 48°. The volatile material was evaporated under vacuum, and the solid was dissolved in water, and its chloride content and radioactivity were determined. The results are in Table 1 (radioactivities are expressed in counts min.$^{-1}$ concn.$^{-1}$).

TABLE 1. *Radioactive measurements on samples from experiment* (1).

Sample	Activity (corr.)
Original 2,3-dichloropropene	27,720
Recovered 2,3-dichloropropene	27,540
sym.-Dichloroacetone [fraction (*i*)]	27,760
1,2,3-Trichloropropene [fraction (*d*)]	27,100
NaCl from partial hydrolysis of 1,2,3-trichloropropene	7,020
HCl from silver chloride precipitated during reaction	350

(2) [3-^{36}Cl]-2,3-Dichloropropene (171 g.) was dissolved in water (*ca.* 85 l.) containing silver perchlorate (0·02M) and perchloric acid (*ca.* 0·5M). Hypochlorous acid (1·312 moles, *ca.* 8·5 l.) was added slowly with stirring during 3 hr. at 27°. After 24 hr., inactive *trans*- (14·04 g.) and *cis*-1,2,3-trichloropropene (14·06 g.) were added to the reaction mixture, which was then stirred for some time to ensure complete mixing. The solution was extracted twice with pentane (*ca.* 5 l.) and the extract was dried and fractionally distilled. There were recovered *cis*-1,2,3-trichloropropene (1·5 g., b. p. 87°/100 mm., n_D^{25} 1·5018) containing neither the isomer nor any other impurity in significant amount, as was shown by examination of the infrared spectrum; and the *trans*-isomer (2 g.), contaminated only with 10% of the *cis*-isomer, as was shown also by infrared spectroscopy. The specific activities of the starting material, and of the recovered samples of *cis*- and of *trans*-1,2,3-trichloropropene were determined; and each was partially hydrolysed to determine also the specific activity of the allylic chlorine atom. Since the *trans*-isomer had not been obtained completely pure, the ratio of allylic to total labelling was determined also on a second specimen, as follows. An intermediate fraction from the distillation (2 g.) was diluted with 12 g. of inactive pure *trans*-1,2,3-trichloropropene, and the mixture carefully fractionated; there was recovered pure *trans*-1,2,3-trichloropropene, b. p. 75°/100 mm., n_D^{25} 1·4956, free from *cis*-isomer. The specific activity of this and of the allylic chloride obtained from it by partial hydrolysis were determined in the usual way. The results are shown in Table 2.

TABLE 2. *Radioactivities of samples from experiment* (2).

Sample	Radioactivity
Original 2,3-dichloropropene	6237
cis-1,2,3-Trichloropropene (diluted)	2069
trans-1,2,3-Trichloropropene (diluted)	2281
LiCl from partial hydrolysis of *cis*-1,2,3-trichloropropene	459
LiCl from partial hydrolysis of *trans*-1,2,3-trichloropropene	259
trans-1,2,3-Trichloropropene (diluted again and further purified)	197
LiCl from partial hydrolysis of purified *trans*-1,2,3-trichloropropene	22·4

DISCUSSION

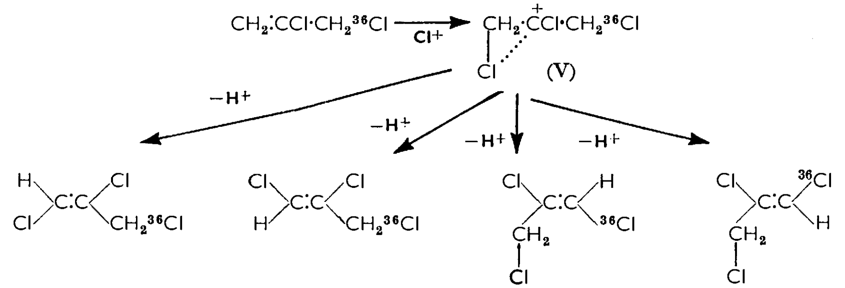
These results illustrate the following points concerning the course of the reactions. The reaction between hypochlorous acid and [3-^{36}Cl]-2,3-dichloropropene gives *sym.*-dichloroacetone, 1,2,3-trichloropropene, other as yet unidentified products, and chloride ion, which is in part derived from the 2-chlorine atom, in part from the hypochlorous acid, and negligibly (at the most 1%) from the 3-chlorine atom. [3-^{36}Cl]-2,3-Dichloropropene recovered after completion of the reaction is unchanged in specific activity: so no direct exchange occurs between the 3-chlorine atom of 2,3-dichloropropene and hypochlorous acid; nor is the initial step of the reaction sufficiently reversible to allow exchange through such a sequence as:

$$Cl^{+} + CH_2{:}CCl{\cdot}CH_2{}^{36}Cl \longrightarrow Cl{\cdot}CH_2{\cdot}\overset{+}{C}Cl{\cdot}CH_2{}^{36}Cl \longrightarrow Cl{\cdot}CH_2{\cdot}CCl{:}CH_2 + {}^{36}Cl^{+}$$

The *sym*-dichloroacetone formed in the reaction has the same specific activity as the starting material, and so is produced with no exchange between the chlorine atoms in the 2- and 3-positions.

From the results given in Table 2, the amounts of *cis*- and of *trans*-1,2,3-trichloropropene formed in the reaction are: *cis*, 3·7%; *trans*, 4·3%. For both of these compounds, partial hydrolysis and examination of the specific activity of the liberated chloride has shown (Table 2) that the proton-loss has occurred mainly from the 3-carbon atom. The ratio of vinylic to allylic labelling is, for the *cis*-isomer, 22 : 78; and for the *trans*-isomer, 11 : 89. That part of the reaction which leads to olefin-formation can therefore be discussed in terms of the following scheme.

Olefin-formation in the reaction between hypochlorous acid and 2,3-dichloropropene.



trans-, allylically labelled 0·5% (VI)

cis-, allylically labelled 0·8% (VII)

trans-, vinylically labelled 3·8% (VIII)

cis-, vinylically labelled 2·9% (IX)

The silver chloride produced in the reaction is derived in part from the attacking hypochlorous acid and in part from the 2-position. It is not significantly derived from the labelled 3-chlorine atom, which therefore does not migrate to the 2-, or therefore to the 1-position, before the main products of the reaction are determined. It seems very probable, therefore, that the main olefinic products (VIII, IX) are derived from an

(X)

$$^{+}CH_2{\cdot}CCl_2{\cdot}CH_2{}^{36}Cl$$

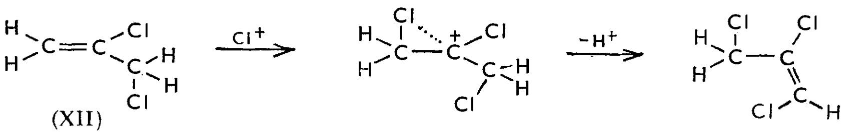
(XI)

unsymmetrical intermediate which can lose a proton, or can combine with water, before undergoing more profound structural changes involving the 3-chlorine atom. For this intermediate, structure (V) is preferred to other possibilities, such as (X) or (XI); essentially because (*a*) electrophilic attack by other reagents occurs with this compound at the 1-carbon atom; and (*b*) if intermediates such as (X) or (XI) were important, we would expect [cf. 2] to isolate without difficulty the compound 2,2,3-trichloropropan-1-ol, through such a reaction as:

$$\overset{+}{C}H_2\cdot CCl_2\cdot CH_2{}^{36}Cl \xrightarrow{H_2O} HO\cdot CH_2\cdot CCl_2\cdot CH_2{}^{36}Cl$$

In fact, this trichlorohydrin has not been detected in the products of the reaction, and cannot form more than a very small part of them.

The *trans*-, vinylically labelled, olefin predominates in the product over the corresponding *cis*-isomer. This suggests that structure (XII) approximately represents the preferred conformation of the dichloropropene as it is being attacked by hypochlorous acid. In this conformation, the 2- and the 3-chlorine atom are by preference as far apart as possible, thus minimising dipolar repulsions between the C–Cl bonds; and proton-loss has a greater chance of occurring in such a way as to leave the two vinylic chlorine atoms *trans* to each other in the product.


(XII)

The present results support the conclusion, reached in a previous investigation,[7] that olefin-formation in these systems is directed in considerable part by stereochemical rather than by polar factors.

Comparison of these experiments with those on allyl chloride [2] suggests that, though the introduction of a 2-chlorine atom has undoubtedly favoured attack on the 1-position, it has not resulted in more prominent participation of the 3-chlorine atom as measured by migration of this to the carbonium ionic centre. Perhaps proton-loss in an overall sense has been favoured in the present reaction by the inductive effect of the 2-chlorine atom, and so this process occurs still more readily after the formation of the carbonium ion, and allows rearrangements involving the 3-chlorine atom less opportunity to compete. Since, however, chloride ion is liberated in the course of the reaction in amount greater than that expected from the amount of dichloroacetone formed, other reactions of the carbonium ion must also be important. The present experiments show that these do not interchange the 3- with the 2-chlorine atom or with the entering chlorine atom, but do not tell us to what extent, if at all, the entering and the 2-chlorine atom become equivalent; and so we defer speculation concerning the stereochemical preference for the *cis*-isomer in the minor product of proton loss, *i.e.*, in the allylically labelled 1,2,3-trichloropropene (VI, VII).

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