# 640. *The Kinetics and Mechanism of Nucleophilic Displacements in Allylic Systems. Part I. Reaction of* 3 : 3-*Dichloroprop*-1-*ene with the Ethoxide Ion.*

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3 : 3-Dichloroprop-1-ene reacts with sodium ethoxide in ethyl alcohol to give, as main products, (i) acraldehyde diethylacetal and (ii) *cis*- and *trans*-1-chloro-3-ethoxyprop-1-ene. The kinetics of these processes, which contribute nearly equally to the total reaction, have now been investigated separately, and have both been shown to be of the kinetic form $-d[RCl_2]/dt = k[RCl_2][OEt^-]$. The latter reaction is interpreted as a synchronous bimolecular substitution with anionotropic rearrangement ($S_N2'$), and the effect of structure on the rate of such reactions is briefly discussed.

3 : 3-DICHLOROPROP-1-ENE (" acraldehyde dichloride "), on reaction with nucleophilic reagents, gives derivatives of its isomer, 1 : 3-dichloropropene. The literature concerning these substitutions accompanied by anionotropic rearrangement is summarised by Huntress (" Organic Chlorine Compounds," John Wiley and Sons, New York, 1948, p. 604). Typically, it was observed by Kirrman, Pacaud, and Dosque (*Bull. Soc. chim.*, 1934, **1**, 860) that, after refluxing 3 : 3-dichloroprop-1-ene with ethyl-alcoholic sodium ethoxide for 15 hours, the products of reaction contain a little of an unidentified propargyl derivative, together with 1-chloro-3-ethoxyprop-1-ene, characterised by its density and refractive index.

This reaction has recently been studied kinetically by Andrews and Kepner (*J. Amer. Chem. Soc.*, 1948, **70**, 3456) and by Smith and King (*ibid.*, 1950, **72**, 95). Their observation, that only part of the chlorine present in the compound is released in the stage which determines the measured rate of the reaction, suggests again that a rearranged material forms at least part of the product.* The bearing of this observation on the mechanism of the reaction was not, however, discussed by either of these groups of workers, although they reported that the reaction was bimolecular, and considerably slower than the corresponding reactions of the isomeric *cis*- and *trans*-1 : 3-dichloropropenes.

Many anionotropic changes are believed to be unimolecular substitutions ($S_N1'$,) in which ionisation of the halide forms a mesomeric cation, which may then react with a nucleophilic reagent in either of two positions. Catchpole, Hughes, and Ingold (*J.*, 1948, 8) have modified and amplified the account of such processes given by Burton and Ingold (*J.*, 1928, 904). The corresponding bimolecular mechanism, involving rearrangement synchronous with bimolecular displacement of halide ions ($S_N2'$), was discussed first by Hughes (*Trans. Faraday Soc.*, 1938, **34**, 185), but the experimental realisation of this possibility has proved somewhat elusive. The first conclusive demonstration of such a reaction mechanism was given by England and Hughes (*Nature*, 1951, **168**, 1002). It has hence become apparent, as was discussed also by Hughes and Ingold (*J. Chim. phys.*, 1948, **45**, 241), that direct bimolecular substitution ($S_N2$) is often preferred to substitution with rearrangement ($S_N2'$) by a factor which is sufficiently large to prevent the product of the latter reaction from being easily detected.

It is well known that *gem*-dihalides are rather resistant to bimolecular nucleophilic substitution. For instance, with alcoholic potassium hydroxide, methylene chloride reacts less rapidly than methyl chloride (Petrenko-Kritschenko and Opotzsky, *Ber.*, 1926, **59**, 2131), and methylene bromide exchanges with bromide ions 50 times less rapidly than does ethyl bromide (de la Mare, Hughes, and Ingold, unpublished work). For this reason, it seemed likely that the bimolecular reactions of 3 : 3-dichloroprop-1-ene would occur less readily than those of allyl chloride. The corresponding $S_N2'$ substitutions with rearrangement should, however, be favoured, seeing that the electron-withdrawing character

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* Direct nucleophilic displacement of chlorine would produce an α-chloro-ether, and such substances characteristically lose chlorine with great rapidity in alkaline solution.

of the $CHCl_2$ group must, by its inductive effect, reduce the density of unsaturation electrons on the 1-carbon atom, and thus render the latter more vulnerable (cf. Hughes and Ingold, *loc. cit.*) to attack by nucleophilic reagents. Taking into account these theoretical considerations, together with the established facts that the reaction with alcoholic sodium ethoxide (*a*) gave the rearranged ether and (*b*) appeared to be bimolecular, we decided to reinvestigate these aspects in some detail, in the hope of demonstrating an $S_N2'$ attack by ethoxide ions.

## EXPERIMENTAL

(*a*) *Materials and Methods.*—3 : 3-Dichloroprop-1-ene was prepared essentially by King and Smith's method (*J. Amer. Chem. Soc.*, 1950, **72**, 3459). The product, after fractionation through a helix-packed column, had b. p. 84·0—84·8°/766 mm., $n_D^{25}$ 1·4456 (Found : C, 32·2; H, 3·7. Calc. for $C_3H_4Cl_2$ : C, 32·4; H, 3·6%). After oxidation with potassium permanganate in acetone, there was recovered from the acidic products, dichloroacetic acid, identified as its *S*-benzylthiuronium derivative, m. p. 173—174°, not changed on admixture with an authentic sample.

*cis*- and *trans*-1 : 3-Dichloropropene were prepared from a commercial sample of the di- and tri-chloropropenes (" Shell DD Soil Fumigant "). This was carefully fractionated, first at atmospheric pressure and then at reduced pressure, giving products with the following constants (*cis*-isomer listed first), which agree well with those recorded by King and Smith (*loc. cit.*), as well as by Hatch, Gordon, and Rust (*J. Amer. Chem. Soc.*, 1948, **70**, 1003) : b. p. 103—104°, 110—112°/760 mm.; 50·3—50·7°/111 mm., 62—63°/136 mm.; $n_D^{25}$ 1·4657, 1·4722. Both these compounds appeared to be substantially free from other isomers, the reactivities of which are considerably different (cf. Smith and King, *loc. cit.*).

*cis*- and *trans*-1-Chloro-3-ethoxyprop-1-ene were prepared by the action of alcoholic sodium ethoxide on the corresponding dichloropropenes, as described by Smith and King (*loc. cit.*). The samples appeared kinetically to be about 97% pure, and had the following constants (*cis*-isomer listed first) : b. p. 64·1—64·6°, 70—71°/102 mm.; $n_D^{25}$ 1·4288, 1·4311 (Found : C, 50·4, 50·3; H, 7·4, 7·5; Cl, 29·7, 29·5. Calc. for $C_5H_9OCl$ : C, 49·8; H, 7·5; Cl, 29·4%).

Hall and Stern (*Chem. and Ind.*, 1950, 775) have shown that the material described as " acrolein diethyl acetal " by Pingert (*Org. Synth.*, **26**, 1) is really 3-ethoxypropaldehyde. We are grateful to these authors, and to the Distillers Co. Ltd., Great Burgh, Epsom, Surrey, for a genuine sample of acraldehyde diethyl acetal, prepared by Fischer and Baer's method (*Helv. Chim. Acta*, 1935, **18**, 514), b. p. 59°/76 mm., $n_D^{20}$ 1·4011, $n_D^{25}$ 1·3990.

Thermostats were of conventional design. Portions of the reaction mixture were sealed in bulbs leaving little dead space, and removed from the thermostat at appropriate intervals for titration either acidimetrically, or potentiometrically with silver nitrate solution. The initial concentrations of organic chloride were determined by weight, and those of alkali by titration with standard acid. Blank determinations were used to allow for reaction during the period of warming to thermostat temperature.

The following are details of a measurement of the rate of reaction of *cis*-1-chloro-3-ethoxyprop-1-ene (0·0465M) with sodium ethoxide (0·515M) in dry ethyl alcohol at 63·7°. Samples (5·53 ml.) were titrated potentiometrically with silver nitrate solution (0·0100M) :

| Time (min.) ............ | 0 | 42 | 86 | 153 | 299 | 417 | 1395 | 1870 | 3270 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|
| Titre (ml. of $AgNO_3$) ... | 0·52 | 0·85 | 1·14 | 1·65 | 2·75 | 3·50 | 9·20 | 11·10 | 16·10 | 26·25 |
| $10^4k_2$ * ..................... | — | 6·40 | 5·79 | 6·06 | 6·21 | 6·06 | 6·13 | 5·98 | 6·08 | — |

Mean values at other temperatures † are: 44·6°, $4·3 \times 10^{-5}$; 85·7°, $9·5 \times 10^{-3}$; 100·0°, $4·28 \times 10^{-2}$.

* All values of $k_2$ quoted in this paper have been calculated by the formula $k_2 = 2·303/t[\text{NaOEt}])$ . $\log_{10} \{(a_\infty - a_0)/(a_t - a_0)\}$, where $a_t$ is the titre at time $t$ minutes; this is appropriate for second-order reactions, such as these, in which the concentration of sodium ethoxide is much greater than that of the organic halide. The quoted values of $a_\infty$ were determined experimentally. The units of $k_2$ are l. g.-mol.$^{-1}$ min.$^{-1}$.

† The abnormal values for the Arrhenius parameters ($B = 10^{17}$ l. g.-mol.$^{-1}$ min.$^{-1}$, $E = 31$ kcals.), and the stereospecificity of this reaction, in which the *cis*-isomer reacts several thousand times more rapidly than the *trans*-compound, will be discussed in future communications.

(*b*) *Products of the Reaction of* 3 : 3-*Dichloroprop*-1-*ene.*—3 : 3-Dichloroprop-1-ene (23 g.) was allowed to react for 17 days at 44·6° with 200 ml. of 1·3M-sodium ethoxide in dry ethyl alcohol. Subsidiary experiments showed that, in this time, 49% of the theoretical amount of chlorine would have been liberated, whereas, in the absence of alkali, less than 0·5% of solvolysis would have occurred. The product was added to 500 ml. of 2N-hydrochloric acid, and extracted with pentane. The pentane extract was washed with water, dried, and fractionated, yielding 2·3 g., b. p. 120—128°, $n_D^{25}$ 1·4280. This had the properties of a mixture of the 1-chloro-3-ethoxyprop-1-enes (Found: C, 49·4; H, 7·4. Calc. for $C_5H_9OCl$: C, 49·8; H, 7·5%), as was confirmed kinetically in the following way. At 85·7°, the reaction of the *trans*-isomer with 0·5N-sodium ethoxide in ethyl alcohol is negligibly slow, whereas more than 99% of the *cis*-isomer is destroyed in 1500 minutes. The following illustrates the rate of development of chloride ion from a solution of the above material (0·0766M, calculated as 1-chloro-3-ethoxyprop-1-ene) with sodium ethoxide (0·5076M) in ethanol at 85·7°:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (min.) | 0 | 68 | 123 | 214 | 312 | 403 | ∞ |
| Titre (ml. of 0·0100M-$AgNO_3$) | 1·28 | 3·60 | 5·12 | 6·88 | 8·30 | 9·08 | 11·08 |
| $k_2$ | — | 0·0085 | 0·0087 | 0·0085 | 0·0087 | 0·0086 | — |

The further rate of development of chloride ion was then measured at 120°, at which temperature all the *cis*-isomer is destroyed in the time allowed for warming to thermostat temperature, as follows:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0 | 21·9 | 71·7 | 92·7 | 117·7 | 143·2 | 164·5 | 186·6 | ∞ |
| Titre (ml. of 0·0100M-$AgNO_3$) | 12·03 | 15·38 | 20·93 | 22·71 | 24·95 | 27·00 | 28·22 | 29·49 | 44·56 |
| $10^4k_2$ | — | 1·99 | 1·79 | 1·74 | 1·75 | 1·75 | 1·70 | 1·69 | — |

The mean rate coefficients thus determined (*cis*-isomer, 0·0086 at 85·6°; *trans*-isomer, 0·000177 at 120°) agree well with those determined independently for pure specimens of these compounds (*cis*-isomer, 0·0095 at 85·7°; *trans*-isomer, 0·000173 at 120°). This product thus contains 25% of the *cis*- and 75% of the *trans*-isomer.

The relatively fast rate of elimination of hydrogen chloride from *cis*-1-chloro-3-ethoxyprop-1-ene made it unlikely that it would be possible to obtain a quantitative estimate of the amount formed in the reaction, or to obtain it in a pure state except by use of prohibitively large quantities of material. In the following experiment, 63·5 g. of 3 : 3-dichloroprop-1-ene were allowed to react to completion (10 days) with 1400 ml. of 1·8N-sodium ethoxide. The product was extracted with pentane from the alkaline solution after dilution with water, dried, and fractionated, giving the following fractions:

| Fraction | B. p./mm. | Wt. (g.) | $n_D^{25}$ | Fraction | B. p./mm. | Wt. (g.) | $n_D^{25}$ |
|---|---|---|---|---|---|---|---|
| 1 | 74—78°/760 | 3·0 | 1·4050 | 7 | 59—61/67 | 4·2 | 1·4163 |
| 2 | 54—56/67 | 2·4 | 1·4009 | 8 | 61—63/67 | 2·6 | 1·4232 |
| 3 | 56—57·5/67 | 5·2 | 1·3995 | 9 | 63—64/67 | 2·4 | 1·4250 |
| 4 | 57·5/67 | 4·9 | 1·4007 | 10 | 64—70/67 | 2·6 | 1·4220 |
| 5 | 57·5—58·5/67 | 4·5 | 1·4025 | 11 | Residue of higher b. p. | 5·8 | — |
| 6 | 58·5—59/67 | 2·2 | 1·4070 | | | | |

The first fraction may have contained propargyl ether, which has $n_D^{25}$ 1·3995, b. p. 82·5°/760 mm., but we were unable to isolate a pure specimen. Fraction 3 was nearly pure acraldehyde diethyl acetal, $n_D^{25}$ 1·3992 (Found: C, 64·6; H, 10·8. Calc. for $C_7H_{14}O_2$: C, 64·8; H, 10·7%). It gave the same colour (within 5%) as an authentic sample, when treated with tryptophan and hydrochloric acid under the conditions of the analytical determination of acraldehyde described below.

Fractions 5—9 contained increasing amounts of *trans*-1-chloro-3-ethoxyprop-1-ene, as judged from the refractive indices. These, together with fraction 10, were treated with 15 ml. of ethanol and 150 ml. of 2N-hydrochloric acid. After 2 hours, the product was extracted with pentane, and the extract was washed with saturated sodium hydrogen sulphite, then with water, dried, and fractionated, giving 6 g., which were steam-distilled with N-hydrochloric acid. The product was dried and fractionated, giving a fraction of $n_D^{25}$ 1·4298 (Found: C, 50·2; H, 8·0. Calc. for $C_5H_9OCl$: C, 49·8; H, 7·5%).

The fractions of higher b. p. (fractions 10 and 11) were complex, and similar to those produced by the action of sodium ethoxide on *cis*-1-chloro-3-ethoxyprop-1-ene. It appears that elimination from this compound is followed by polymerisation or condensation with other materials present in the solution. No pure fraction was obtained, the b. p. at atmospheric pressure rising steadily to >220°, and this material was not investigated further.

In order to demonstrate that, from incomplete reaction with sodium ethoxide, unchanged 3 : 3-dichloroprop-1-ene can be recovered, 40 g. of this substance were treated with excess of 0·98N-sodium ethoxide at 85·4° for a time sufficient to allow *ca.* 35% release of chlorine from the compound. There was recovered in the usual way *ca.* 5 g., b. p. 83—83·6°, $n_D^{25}$ 1·4439 (Calc. 1·4456) (Found: C, 34·3; H, 3·8. Calc. for $C_3H_4Cl_2$: C, 32·4; H, 3·6%), and hence it seems probable that the product is an azeotrope containing about 10% of 1-chloro-3-ethoxyprop-1-ene, as would agree both with the analytical data and with the refractive index. The following experiment shows the rate of solvolysis of this substance in 50% alcohol–water at 85·5°, 5·53-ml. portions being titrated with alkali:

| Time (min.) | 0 | 6 | 15 | 24 | 32 | 48 | 62 | 110 | 172 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|
| Titre (ml. of 0·01996N-alkali) | 1·79 | 2·60 | 3·81 | 4·89 | 5·85 | 7·45 | 8·80 | 11·90 | 14·49 | 17·41 |
| $10^3k_1$ * | — | 8·9 | 9·2 | 9·2 | 9·4 | 9·4 | 9·6 | 9·5 | 9·8 | — |

* Values of $k_1$ have been calculated by using the formula $k_1 = (2{\cdot}303/t)\log_{10}(a_\infty - a_0)/(a_t - a_0)$, where $a_t$ is the titre at time $t$ minutes, and are given in units min.$^{-1}$.

Authentic 3 : 3-dichloroprop-1-ene reacted at an almost identical rate; herewith are the data at 85·3°:

| Time (min.) | 0 | 6 | 12 | 18 | 24 | 32 | 41 | 47 | 57 | 131 | 183 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Titre (ml. of 0·01788N-alkali) | 1·98 | 3·11 | 3·99 | 4·98 | 5·85 | 6·75 | 8·12 | 8·82 | 9·91 | 15·63 | 17·90 | 21·60 |
| $10^3k_1$ | — | 9·9 | 9·0 | 9·2 | 9·2 | 8·7 | 9·2 | 9·2 | 9·1 | 9·1 | 9·1 | — |

It is certain, therefore, that the product recovered in this experiment was substantially the unchanged starting material.

(*c*) *Kinetics of the Reaction of* 3 : 3-*Dichloroprop*-1-*ene*.—(i) *Rate of formation of acraldehyde diethylacetal.* Many of the recorded methods for the detection and estimation of acraldehyde are not specific. Circle, Stace, and Boruff (*Ind. Eng. Chem. Anal.*, 1945, **17**, 259) have, however, recently developed a method, involving condensation with tryptophan in acid solution, suitable for the colorimetric estimation of this substance, acetaldehyde and other common aldehydes giving no interfering colour. The following procedure, which is substantially that recommended by the above workers, was therefore adopted. A sample (2 ml., in alcohol, containing less than 0·01M-acraldehyde diethyl acetal) was added to 3 ml. of tryptophan solution (0·7 g./l. in 0·02N-HCl). Ice-cold, 12N-hydrochloric acid (10 ml.) was added, the colour was allowed to develop for 2 hours in the dark at room temperature, and its intensity then measured in a 1-cm. cell in a Hilger Spekker absorptiometer, with a yellow-green filter No. 605, and compared with the colour obtained from a standard alcoholic solution of acraldehyde diethylacetal. This substance is rapidly hydrolysed to acraldehyde under the conditions of measurement, and in our hands gave a colour slightly more intense (by about 10%) than that given by commercial samples of acraldehyde treated in similar fashion.

Neither 3 : 3-dichloroprop-1-ene nor the 1-chloro-3-ethoxyprop-1-enes gave any colour with the reagent or disturbed the development of colour. It was found, however, that the complex products obtained by the prolonged action of sodium ethoxide on *cis*-1-chloro-3-ethoxyprop-1-ene interfered slightly with the infinity determinations. The following experiment shows the rate of development of chloride and of material analysing as acraldehyde from *cis*-1-chloro-3-ethoxyprop-1-ene (0·0525M) and sodium ethoxide (0·617M) in alcohol at 100°, the initial tube being taken after a warming-up time of 10 minutes:

| Time (min.) | 0 | 8 | 12 | 18 | 23 | 28 | 90 | 213 | ∞ |
|---|---|---|---|---|---|---|---|---|---|
| Chloride (%) | 23·1 | 36·3 | 42·8 | 50·9 | 56·1 | 61·2 | 89·8 | 98·3 | 100 |
| " Acraldehyde " (%) | 0·0 | 0·0 | 0·0 | 0·0 | 0·0 | 0·0 | 4·3 | 18·4 | 38·4 |

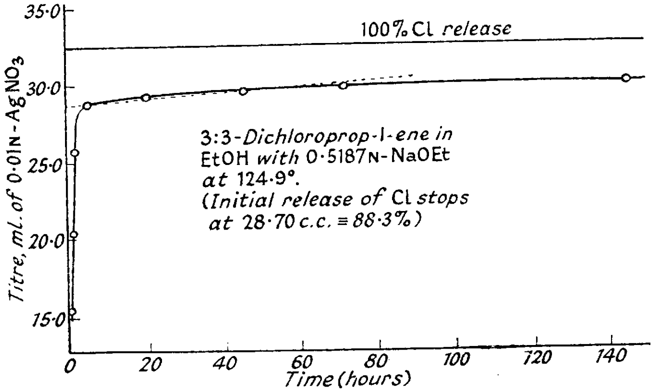
It is clear that the interference becomes important only towards the end of the reaction, and hence the infinity determinations for the corresponding reaction of 3 : 3-dichloroprop-1-ene have been corrected slightly ($\ngtr$10%) to allow for this disturbance. The following shows the rate of production of acraldehyde diethylacetal from 0·0514M-3 : 3-dichloroprop-1-ene and 0·549M-sodium ethoxide in alcohol at 24·9°. The initial tube was taken after a warming-up time of 20 minutes:

| Time (min.) ...... | 0 | 177 | 239 | 310 | 377 | 826 | 1068 | 2278 | ∞ (obs.) | ∞ (corr.) |
|---|---|---|---|---|---|---|---|---|---|---|
| Spekker reading ... | 0·103 | 0·186 | 0·363 | 0·409 | 0·474 | 0·850 | 1·027 | 1·680 † | 2·824 † | 2·589 |
| $10^4k_2$ * ............... | — | 8·43 | 8·66 | 8·11 | 8·12 | 8·28 | 8·31 | 8·44 | — | — |

* These values of $k_2$ have been calculated as previously described, Spekker readings being used in place of titres. The observed infinity value was corrected by using a determination of the colour produced from a known quantity of the *cis*-ether under the same conditions. It was assumed that all the reaction not leading initially to acraldehyde diethylacetal is equally partitioned between *cis*- and *trans*-chloro-3-ethoxyprop-1-ene; any error arising from this assumption will have a negligible effect on the calculated rate coefficients, since the correction itself is small.

† Measured after appropriate dilution.

These rate coefficients refer to the total reaction, as in the analogous case discussed by Cooper, Hughes, and Ingold (*J.*, 1937, 1280). Values determined at 85·4° (mean $10^4k_2 = 83·5$) enable one to calculate the activation energy as *ca.* 27 kcal. The dependence of second-order rate coefficients on concentration of sodium ethoxide is shown by the following relative values at 85·4°: 0·52N-NaOH, 1·0; 0·19N-NaOH, 1·1; 0·06N-NaOEt, 1·2. The rate of reaction is therefore dependent directly on the concentration of sodium ethoxide, with the usual slight modification due to a negative salt effect.



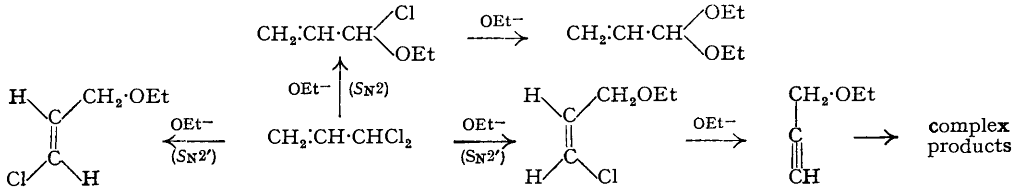
The percentages of acraldehyde diethyl acetal produced in the above reactions were 51·6% at 64·9° and 42·5% at 85·4°. These results indicate that the proportion of reaction proceeding by the $S_N2$ route to give acraldehyde diethyl acetal decreases with increased temperature.

(ii) *Rate of development of chloride ion.* The composite bimolecular reaction of ethoxide ions with 3 : 3-dichloroprop-1-ene to yield derivatives of acraldehyde, as well as the 1-chloro-3-ethoxyprop-1-enes, releases between 100% and 50% of the theoretical amount of chlorine from the organic dichloride, depending on the ratio in which the component reactions contribute. To calculate a true rate constant for the production of chloride ion, it would be necessary to know the amount of chloride released when this reaction is completed. Unfortunately, the *cis*-chloro-ether, which is one of the products of the $S_N2'$ reaction, undergoes, in the presence of ethoxide ion, elimination of hydrogen chloride at a rate similar to that of its formation from 3 : 3-dichloroprop-1-ene. Hence, determinations of chloride cannot easily be used to estimate the " infinity " value which is required for the calculation of true rate constants. For this reason, details are given of the rate of production of chloride ion only to show the existence of *trans*-1-chloro-3-ethoxyprop-1-ene in the final stages of the reaction. The figure shows the rate of development of chloride ion from 0·0294M-3 :3-dichloroprop-1-ene and 0·519N-sodium ethoxide at 124·9°. After approx. 4 hours, the initially rapid production of chloride had ceased, and the subsequent rate corresponded to a second-order coefficient of 0·00020. This agrees well both with the value obtained for the authentic *trans*-1-chloro-3-ethoxyprop-1-ene (0·000173 at 120°) and with that obtained for the ether isolated from the reaction product (0·000177 at 120°). The initial rapid production of chloride ion ceases at 88·3% release of chlorine, which corresponds with the production from 3 : 3-dichloroprop-1-ene of 23·4% of *trans*-ether.

(iii) *Rate of solvolysis.* Solvolysis of 3 : 3-dichloroprop-1-ene is too slow to allow the reaction to be followed conveniently for more than the initial part of the reaction; *e.g.*, after reaction for 1000 minutes at 85·6°, 2·28% of chlorine is released from the compound, and 0·62% of acraldehyde diethyl acetal is produced. In the presence of 0·5N-sodium ethoxide under the same conditions, *ca.* 84% of chlorine and *ca.* 40% of acraldehyde diethyl acetal would have been produced. The solvolysis is thus a negligible factor in determining the kinetics of, and the products from, the reaction in the presence of sodium ethoxide, which is therefore a bimolecular process.

## DISCUSSION

(i) *Products of the Reaction.*—In view of the above experimental findings, the following scheme may be written for the reaction of 3 : 3-dichloroprop-1-ene with sodium ethoxide in ethyl alcohol :



Our most important task was to confirm that 1-chloro-3-ethoxyprop-1-ene forms a part of the product of the reaction. Conclusive evidence has now been given for the formation both of the *cis*- and of the *trans*-isomer of this substance. The *trans*-isomer, being the more stable to alkali, is the more easily isolated. The *cis*-isomer was identified only as a product of partial reaction, mixed with its *trans*-isomer, but reacted at a characteristic rate with alcoholic sodium ethoxide at 85·6°.

The weight of *trans*-ether isolated, in the experiment in which 11 g. of the dichloride should have undergone reaction, was 2·3 g., representing about 20% of the total reaction. One might presume that an equal quantity had been lost in intermediate fractions, and by decomposition of the *cis*-ether. The remainder of the reaction results in the production of acraldehyde diethyl acetal, which was isolated almost pure by careful fractionation of the product obtained when the reaction was forced to completion. The emphasis laid in earlier literature (cf. Huntress, *op. cit.*) on rearrangements accompanying bimolecular reactions of this dichloride is thus unjustified : both normal and rearranged products are important components of the reaction product; we shall also document them for the corresponding unimolecular processes.

(ii) *Mechanisms involved in the Reaction.*—The solvolysis of 3 : 3-dichloroprop-1-ene has been shown to be negligibly slow, compared with its reaction with ethoxide ions. The latter process, which results in the formation of acraldehyde diethyl acetal and the 1-chloro-3-ethoxyprop-1-enes, must therefore be almost exclusively of the second order.* Acraldehyde diethyl acetal is clearly the result of normal bimolecular substitution ($S_N2$), proceeding at the slow rate expected for a *gem*-dichloride, followed by rapid liberation of the second chlorine atom. The 1-chloro-3-ethoxyprop-1-enes form, however, a substantial part (40—50%) of the product. In view of the dependence of the rate of reaction on the concentration of alkali, these products of rearrangement must also be produced in a second-order process, which we consider to be a bimolecular substitution with anionotropic rearrangement ($S_N2'$). This conclusion is further strengthened by the kinetically simpler results for the corresponding reaction with sodium thiophenoxide described in the following paper.†

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* This is shown also by the fact that, salt effects being neglected, the second-order rate-coefficients for the total reaction (measured by following the production of acraldehyde diethyl acetal as described above) do not vary with the concentration of sodium ethoxide.

† It might be supposed that the initial bimolecular process involved the removal of a proton : $CH_2{:}CH{\cdot}CHCl_2 + OEt^- \longrightarrow CH_2{:}CH{\cdot}CCl_2^-$. In the resulting carbanion, the charge would be distributed by mesomerism : $CH_2{:}CH{\cdot}CCl_2^- \longleftrightarrow {}^-CH_2{\cdot}CH{:}CCl_2$. There seems to be no reason why the presence of this charge should in any way facilitate the attachment of an ethoxy-group in the 3-position; indeed, it must retard any further approach by a nucleophilic reagent, while encouraging attachment of a proton to form the prototropically rearranged isomer, $CH_3{\cdot}CH{:}CCl_2$ which is very stable to alkali, particularly at low temperatures (cf. Smith and King, *loc. cit.*). We have not been able to isolate this compound from the reaction product, though we consider that a small amount ($\not> 10\%$) may possibly be produced in the reaction.

Considering, in a general way, substitutions under bimolecular conditions of the type : $CH_2{:}CH{\cdot}CHR{\cdot}X + Y^-$, it has already been observed, as by England and Hughes (*loc. cit.*), that, for the commoner allyl structures (*e.g.*, R = Me), when these are attacked by the usual nucleophilic reagents (*e.g.*, Y = $OH^-$, $Br^-$, $Cl^-$, $OEt^-$), the direct ($S_N2$) substitution, compared with rearrangement ($S_N2'$), is favoured by a factor of the order of $10^2$. Various possible methods exist for rendering the latter process experimentally accessible, including the following : (*a*) For the symmetrical case (Y = X), the $S_N2$ reaction regenerates the starting material, and the $S_N2'$ reaction may be studied directly, as by England and Hughes (*loc. cit.*; R = Me, X = Y = Br). (*b*) R may be altered in such a way as to favour the $S_N2'$ mechanism ; and if at the same time the $S_N2$ process is hindered, the former mechanism may become predominant, as in the reaction studied in this investigation (R = Cl, Y = OEt) ; we are extending use of this principle to the investigation of related systems. (*c*) R may be altered in such a way as to inhibit sterically the $S_N2$ reaction, so that the $S_N2'$ process becomes predominant, independently of its polar requirements. Such a case is at present under investigation in these laboratories by Mr. P. C. Merriman (R = $Bu^t$). (*d*) The relative reactivities of the reagent Y for the two positions may be altered in such a way as to favour the $S_N2'$ mechanism. Kepner, Winstein, and Young (*J. Amer. Chem. Soc.*, 1949, **71**, 115) gave a possible example of this behaviour [R = Et, Y = $CH(CO_2Et)_2^-$], though doubt has been cast (*e.g.*, by Dewar, *Bull. Soc. chim.*, 1951, **18**, C 42) on the interpretation of the latter reaction as following the $S_N2'$ mechanism.

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