641. *The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part II.* The Reactions between* 3 : 3-*Dichloroprop*-1-*ene and the Thiophenoxide Ion.*

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3 : 3-Dichloroprop-1-ene reacts with sodium thiophenoxide by a reaction which has the kinetic form $-d[RCl_2]/dt = k[RCl_2][SPh^-]$, releases 81% of chlorine from the dichloride, and produces (together with a diphenylthiopropene), a mixture of *cis*- and *trans*-1-chloro-3-phenylthioprop-1-ene in *ca.* 38% yield. It is considered that these latter substances are formed by a bimolecular nucleophilic substitution with rearrangement (S_N2').

In Part I * it was shown that 3 : 3-dichloroprop-1-ene reacts with ethoxide ions by a bimolecular mechanism to form, together with products of normal substitution (S_N2), those involving anionotropic rearrangement (S_N2'). The reaction was, however, composite, and one of the products (*cis*-1-chloro-3-ethoxyprop-1-ene) rather rapidly underwent further elimination of hydrogen chloride under the conditions of the rate measurements. Furthermore, it was suspected, though not proved, that a small amount of prototropic rearrangement (forming 1 : 1-dichloroprop-1-ene and its products of decomposition) accompanied the main reaction.

It seemed desirable, therefore, to examine the reaction of 3 : 3-dichloroprop-1-ene with a reagent less likely to promote prototropic changes or elimination reactions. The thiophenoxide ion proved eminently suitable. This reagent has a small tendency to attach itself to a proton; *e.g.*, the acid dissociation constant of thiophenol has pK = 9·3 n 95% ethanol (Schwartzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 1360), compared

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* Part I, preceding paper.

with that of phenol, $pK = 12{\cdot}8$ in 95% ethanol (*idem, ibid.*) or of ethyl alcohol, $pK_{\text{auto}} = 19{\cdot}0$ (cf. Remick, " Electronic Interpretation of Organic Chemistry," Wiley and Sons, N.Y., p. 324). On the other hand, its reactivity towards a carbon centre is much more facile than that of either the ethoxide or the phenoxide ion. This high reactivity (cf. Quayle and Royal, *J. Amer. Chem. Soc.*, 1942, **64**, 227) applies also to nucleophilic displacement by RS^- ions at aromatic centres (Hodgson and Handley, *J. Soc. Chem. Ind.*, 1927, **46**, 435T; cf. Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 273), indicating that the phenomenon is not a property specifically of a saturated carbon atom. With these facts in mind, the kinetics and products of the reaction between 3 : 3-dichloroprop-1-ene and the thiophenoxide ion have been examined.

EXPERIMENTAL

Solutions of sodium thiophenoxide were prepared by adding the theoretical quantity of redistilled thiophenol (L. Light and Co.) to a solution of sodium ethoxide in ethyl alcohol. Conventional methods were used in following the rate of disappearance of this ion; aliquots of the reaction mixture were added to excess of standard acid, and back-titrated with standard alkali, bromophenol-blue being used as indicator. Other materials were as described in Part I (*loc. cit.*).

The following are details of a typical rate-measurement. Thiophenol (2·66 g.) was added to 255 ml. of 0·0953N-sodium ethoxide in ethyl alcohol, and 3 : 3-dichloroprop-1-ene (1·139 g.) was made up to 250 ml. with this solution. Aliquots of 5·53 ml. were added to 10 ml. of 0·1730N-hydrochloric acid, and back-titrated with 0·02025N-sodium hydroxide. The initial sample was taken after it had been allowed to warm to the temperature of the thermostat (24·7°) for ten minutes :

Time (min.)	0	160	252	313	386	438	1382	1692	3155	∞
Titre (ml. NaOH)	17·46	19·06	19·82	20·31	20·90	21·32	26·10	27·28	30·69	35·46
10^3k_2	—	6·53	6·35	6·34	6·42	6·51	6·43	6·62	7·00	—

Further tubes from the same batch being used, the following mean velocity coefficients were obtained : at 45·2°, $10^3k_2 = 64{\cdot}4$; at 65·3°, $10^3k_2 = 470$. From these values are derived the following Arrhenius parameters : $E = 21{\cdot}2$ kcal., $\log_{10} B$ [*] = 13·34.

The runs were demonstrably of the second order, as is also shown by the results of varying the concentration of thiophenoxide ion at 45·2°; $SPh^- = 0{\cdot}0883$, $10^3k_2 = 64{\cdot}4$; $SPh^- = 0{\cdot}2176$, $10^3k_2 = 54{\cdot}2$. The small " dilution " (negative salt) effect characteristic of this class of second-order reactions in alcohol (cf. Hughes, Ingold, Masterman, and McNulty, *J.*, 1940, 903) is also manifest in these results.

The percentage of chlorine released from the dichloride in the above experiments was 81. Confirmation of this value was obtained by direct estimation of chloride at completion of the reaction, by potentiometric titration after organic substances had been removed by extraction from acid solution. Values obtained at different temperatures by this method were : 85°, 81%; 65°, 80%; 45°, 81%. These values reflect the proportions to which the S_N2 and the S_N2' reactions (releasing 2 and 1 equiv. of chlorine, respectively) contribute to the total process; it is clear that these processes have almost the same activation energy.

A single measurement was made of the rate of reaction of 3 : 3-dichloroprop-1-ene (0·069M) with sodium phenoxide (0·869M) in ethyl alcohol at 100°. Reaction had virtually ceased after the liberation of 89% of chlorine from the compound : the second-order rate coefficient for the whole process was 0·030 l. g.-mol.$^{-1}$ min.$^{-1}$.

Products of Reaction.—For reference *trans*-1-chloro-3-phenylthioprop-1-ene was prepared from *trans*-1 : 3-dichloropropene (1·5 g.), which was dissolved in a solution containing 15 ml. of thiophenol in 150 ml. of N-sodium ethoxide in ethyl alcohol. The reaction mixture was left overnight, and was then diluted with water and extracted three times with pentane. The extract was washed with water, dried, and evaporated to small bulk. On cooling to −80°, white crystals separated, which were recrystallised from pentane, and distilled *in vacuo* giving a product, b. p. 260°/770 mm. (decomp.), n_D^{25} 1·5900, m. p. 5° (Found : C, 58·8; H, 5·5; S, 17·0; Cl, 18·9. C_9H_9SCl requires C, 58·5; H, 4·9; S, 17·35; Cl, 19·25%). From *cis*-1 : 3-dichloro-

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[*] Values of k_2 and B, units l. g.-mol.$^{-1}$ min.$^{-1}$, are calculated from the formulæ $k_2 = Be^{-E/RT} = [2{\cdot}303/t(a - x_\infty)] \log_{10} x_\infty(a - x_t)/a(x_\infty - x_t)$ where a is the initial concentration of SPh^- and x_t is the concentration of HCl produced by the reaction at time t; this is appropriate for calculation of second-order rate-coefficients for the total reaction.

propene there was obtained similarly cis-1-*chloro*-3-*phenylthioprop*-1-*ene* as an oil, b. p. 260°/770 mm. (decomp.), n_D^{25} 1·5891 (Found: C, 57·9; H, 4·7%).

When 27 g. of 3 : 3-dichloroprop-1-ene were mixed with 800 ml. of 0·63N-sodium thiophenoxide, the solution became warm, and sodium chloride was precipitated. The reaction was completed at 60°, and the product was poured into water and extracted with pentane. The washed and dried extract was fractionated at reduced pressure; a middle fraction, 6·6 g., had b. p. 76°/*ca.* 0·5 mm., n_D^{25} 1·5888 (Found: C, 58·8; H, 5·0; S, 16·9; Cl, 19·2%), of the same m. p. (−11°) as an equimolar mixture of *cis*- and *trans*-1-chloro-3-phenylthioprop-1-ene. After two recrystallisations from pentane at low temperature, there were obtained 2 g. of material, n_D^{25} 1·5901 (Found: C, 59·1; H, 5·1; S, 17·0; Cl, 18·9%), m. p. 5° unchanged on admixture with an authentic specimen of *trans*-1-chloro-3-phenylthioprop-1-ene.

The higher-boiling material was statically distilled at *ca.* 0·03 mm., giving 27 g. of material, n_D^{25} 1·6456, and leaving a residue of tar. A middle fraction, n_D^{25} 1·6479, from this material gave the following analysis: C, 68·5; H, 5·7; S, 25·2 ($C_{15}H_{14}S_2$ requires C, 69·8; H, 5·4; S, 24·8%) and hence, by analogy with the formation of $CH_2{:}CH{\cdot}CH(OEt)_2$ from 3 : 3-dichloroprop-1-ene and ethoxide ions (Part I) is 3 : 3(?)-*diphenylthioprop*-1-*ene*, $CH_2{:}CH{\cdot}CH(SPh)_2$, a final product of the S_N2 displacement of chlorine. This formulation is also consistent with the ultra-violet absorption spectrum of the compound, which was determined by Dr. D. P. Craig, using a Carey recording spectrophotometer. In alcoholic solution, there was a maximum molecular extinction coefficient ($\varepsilon_{max.}$) of 13,800 at 2515 Å, with a shoulder on the absorption curve at about 2600 Å. The compound $CH_3{\cdot}CH(SPh)_2$ has $\varepsilon_{max.} = 10,000$ at 2560 Å (Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 2889), and the absorption curves of the two compounds have very similar shapes.

DISCUSSION

The reaction of 3 : 3-dichloroprop-1-ene with the thiophenoxide ion follows the kinetic law $-d[RCl_2]/dt = k[RCl_2][SPh^-]$. It is therefore a bimolecular displacement, a large component of which leads to the formation of the rearranged thio-ether $SPh{\cdot}CH_2{\cdot}CH{:}CHCl$. This is to be interpreted, in our opinion, as the result of a bimolecular nucleophilic displacement with anionotropic rearrangement, S_N2'. The present example is kinetically less complex than the corresponding reaction involving ethoxide ions (Part I, *loc. cit.*), since the initial products are stable in the presence of the reagent. It is possible to determine with reasonable accuracy the Arrhenius parameters of the individual processes, which both have an activation energy of 21·2 kcal.; the values of $\log_{10} B$ are, for the S_N2 and S_N2' reactions respectively, 13·20 and 12·92. Thus the non-exponential term in the Arrhenius equation for the reaction which leads to rearrangement shows no particular abnormality, being within the range of values typical of reactions between negative ions and neutral molecules, in accordance with the similar results of England and Hughes (*Nature*, 1951, **168**, 1002).

The following figures illustrate the relative contribution of the S_N2 and S_N2' processes to the reaction of 3 : 3-dichloroprop-1-ene with various reagents:

Reagent	OEt^-	OPh^-	SPh^-
Total rate of substitution, k_2 (l. g.-mol.$^{-1}$ min.$^{-1}$)	0·036	0·030	8·73
% Cl released	*ca.* 70	89	81
% S_N2'	*ca.* 40	22	38

The data are not extensive enough to allow generalisation, but it seems that the relative ease of attack by the nucleophilic reagent at the two positions is not very critically dependent on the nature of the anion.* Consequently, this compound, in such reactions, is likely usually to give a mixture containing a substantial quantity of both normal and rearranged product. It is to be noted that, as far as can be deduced from the present experiments, *cis*- and *trans*-olefinic compounds are produced in approximately equal amount by the S_N2' reaction.

The above comparison of the total rate of substitution illustrates the exceptional

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* It is not possible to be certain whether the comparable solvolysis of this compound with ethyl alcohol is uni- or bi-molecular: but the results given in Part I make it clear that the use of a neutral molecule replacing an anion as the nucleophilic reagent does not to any great degree, if at all, favour the rearrangement, since a good proportion of acraldehyde diethylacetal is also produced in the solvolysis.

nucleophilic power of the thiophenoxide ion towards a carbon centre. The nucleophilic power of anions is often associated with their affinities for a proton, but comparison indicates the limitations of this correlation (cf. also Hughes, *Quart. Reviews*, 1951, **5**, 245), since compounds of the type RSH are much stronger acids than the corresponding compounds of the type ROH.

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